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Subject : Notification letter for review process ID. No. 2016-02-917
Encl. : -

Yogyakarta, 23 February 2016

Dear Mr. Muhammad Cholid Djunaidi,
Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University (UNDIP), Jl. Prof. Soedarto, S.H., Tembalang-Semarang, Indonesia

We would like to inform you that we have received the article you have submitted to *Indones. J. Chem.* journal entitled:

Synthesis of a Novel Carrier Thiazoethyl Methyl Eugenoxi Acetate from Eugenol with Bulk Liquid Membrane (BLM) Technique

written by:

Muhammad Cholid Djunaidi, Pratama Jujur Wibawa, and Ratna Hari Murti

Your paper has been assigned with an ID of 2016-02-917. Please refer to this ID whenever you communicate with our Editorial Office in the future.

Your paper will undergo the normal review process of the journal. The process normally takes 2 to 5 months to complete depending on the number of rounds the reviews needs to take place. For the 1st round review, it will take approximately 8 weeks. Please do expect slight delay if the review period overlaps with a long holiday.

Once again, thank you very much for your submission to the *Indones. J. Chem*. If your article is eligible, then it will be published in the next edition of Indonesian Journal of Chemistry (*Indones. J. Chem.*).

Sincerely yours,

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Yogyakarta, 10 Maret 2016

Kepada Yth.,

Muhammad Cholid Djunaidi

Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University (UNDIP), Jl. Prof. Soedarto, S.H., Tembalang-Semarang, Indonesia

Dengan hormat,
Bersama ini disampaikan hasil penilaian awal dari tim editor untuk naskah artikel yang Saudara kirim dengan judul:

> ***Synthesis of a Novel Carrier Thiazoethyl Methyl Eugenoxi Acetate from Eugenol with Bulk Liquid Membrane (BLM) Technique***

yang ditulis oleh:

> Muhammad Cholid Djunaidi, Pratama Jujur Wibawa, and Ratna Hari Murti

dinyatakan belum dapat diteruskan pada tahap penilaian artikel oleh reviewer *Indones. J. Chem.* dengan pertimbangan sebagai berikut :

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SYNTHESIS OF A NOVEL CARRIER THIAZOETHYL METHYL EUGENOXI ACETATE FROM EUGENOL WITH BULK LIQUID MEMBRANE (BLM) TECHNIQUE

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Abstract. The research on synthesis and using of a Novel Carrier Thiazoethyl Methyl Eugenoxi Acetic Acid (TMEAA) has conducted to selective transport metals of Cu (II), Cd (II) and Cr (III) with Bulk Liquid Membrane Technique (BLM). TMEAA was synthesized from eugenol. Eugenol was acidified into eugenoxi acetic acid and then followed by esterified using 4-methyl-5-thiazoethanol. Analysis of the results were performed by GC MS, FTIR and ^{1}H NMR. TMEAA that tobtained was liquid, viscous, blackish brown, fragrant with a yield of 88%. This compound was soluble in benzene and chloroform but insoluble in methanol. The results of GC-MS analysis showed a single peak with a retention time of 26.5 minutes with an area of 100%, while disappearance of the acid absorption of 1727 cm^{-1} in the FTIR spectra indicate that formation ester groups was occured. TMEAA was used as carrier technique BLM in chloroform to transport Cu (II), Cd (II) and Cr (III). The results showed that TMEAA was more selectivity toward Cu(II) and Cd(II) than Cr(III). The research proved that the group N and S of TMEAA selective for Cu (II) and Cd (II).

Keywords: BLM, selective transport, Thiazoethyl Methyl Eugenoxi Acetic Acid, eugenol.

Abstrak. Telah dilakukan penelitian tentang sintesis dan penggunaan Senyawa Carrier Tiazoetil Metil Eugenoksi Asetat untuk transpor selektif logam-logam Cu(II), Cd(II) dan Cr(III) menggunakan Teknik Membran Cair Ruah (BLM) dan menentukan selektifitas carrier tersebut. TMEAA disintesis dari eugenol menjadi asam eugenoksi asetat dilanjutkan dengan esterifikasi 4-metil-5 tiazoetanol. Analisis hasil dilakukan dengan GC-MS, FTIR dan ^{1}H NMR. TMEAA yang diperoleh berbentuk cair, kental, berwarna coklat kehitaman, berbau harum dengan rendemen reaksi 88%. Senyawa ini larut dalam benzena dan kloroform, namun sukar larut dalam metanol. Hasil analisa GC-MS menunjukkan satu puncak dengan waktu retensi 26,5 menit dengan luas area 100%, sementara hilangnya serapan asam pada 1727 cm^{-1} pada spektra FTIR menunjukkan terbentuknya gugus ester. TMEOA hasil sintesis digunakan sebagai *carrier* teknik BLM dalam pelarut kloroform untuk transpor Cu (II), Cd (II) dan Cr (III). Hasil yang diperoleh TMEAA lebih selektif terhadap Cu (II) dan Cd (II) daripada Cr (III). Hasil penelitian membuktikan bahwa gugus N dan S dari TMEAA selektif terhadap Cu(II) dan Cd(II).

Kata Kunci: BLM, selective transport, Tiazoetil Metil Eugenoksi asetat, eugenol.

INTRODUCTION

Separation of heavy metals with liquid membrane is one of the development solvent extraction method that can be used for the recovery of heavy metals from wastewater, valuable metal exploration from mining of material and for the purpose of analysis. Advantages of liquid membrane system are selective and efficience, the little consume of solvent, can be carried out continuously in a single unit operation, simple, and inexpensive [1]

The stability of complex between metal and carrier compound determine the selectivity of separation using liquid membrane technique. The stability of the complex is determined by several factors, including the type of donor atoms (active group) owned carrier compound that suitable with a metal electron configuration [2]. The use of a carrier compound in liquid membrane techniques is to improve the efficiency and selectivity of transport [3].

Eugenol contained in clove oil, has three active groups: allyl, methoxy and hydroxyl. From the hydroxyl groups can be substituted by more selective groups. Make eugenol has potential as a selective compound carrier.

Eugenol has been widely used for the separation of heavy metals, including eugenol polymer (polyeugenol) used to adsorb ion Fe (III) [4,5], as a functional polymer in membrane in situ [6] and in particles membrane [7].

Eugenol derivatives with N donor atoms from pyridyl carbinol was selective to borderline metal (Cu^{2+}) [8]. The working principle of the compound carrier is based by theory HSAB (grouping acid-base based on the hardness and softness) which states that, in general, ion hard metals (such as alkali metals, alkaline earth, and Cr^{3+}) form a stronger complex with donor atoms hardware (such as O), ion soft metals (such as Cd^{2+}) with donor atoms of soft (such as S) and metal ions borderline (such as Cu^{2+}) with donor atoms borderline (such as N) [2]. A carrier compound that has active group nitrogen atom (N) and sulfur atom (S) is expected to selective to Cu^{2+} and Cd^{2+}.

In this research we will recovered metal ions Cr^{3+}, Cd^{2+} and Cu^{2+} from waste simulation using Thiazoethyl Methyl Eugenoxi Acetic Acid that synthesized from eugenol using Bulk Liquid Membrane BLM (Bulk Liquid Membrane) techniques. BLM is a simples of liquid membrane and usually used for the study in the liquid membrane transport processes.

EXPERIMENTAL SECTION

Materials

The materials were purchased from SIGMA-Aldrich, Eugenol, BF_3-diethylether while other reagents were purchased from E Merck, Germany: $SOCl_2$, 4-methyl-5-thiazoleethanol, NaOH, chloroacetic acid, $CrCl_3.\ 6H_2O$, $CuCl_2.2H_2O$, $CdCl_2.H_2O$. Chloroform, Methanol, Diethylether and demineralized water were purchased from Bratachem.

Instrumentation

The instruments used to characterization of TMEAA in this study were FTIR Spectrophotometer (Shimadzu 8201PC), and GC MS (Shimadzu QP2010S), NMR ^1H JEOL-MY60, analytical balance (Mettler Tolendo AB54-S), Atomic Absorption Spectrophotometer (Perkin Elmer), pH meter (HACH E C20).

Equipments: Laboratory Glassware and a set of tools BLM (U tube, Fig 1).

Procedure

Liquid Membrane Preparation

0.7 g thiazoethyl methyl eugenoxi acetic acid (TMEAA) was dissolved in 30 mL of chloroform.

Recovery process

A solution of 30 mL TMEAA was poured in the U tube was placed between the feed phase and phase receiver each 13 mL, then stirred for 24 hours.

Measurement of pH

After the feed phase and stripping phase through the mixing process for 24 hours, the pH was measured by pH meter on both side.

Analysis by AAS

Analysis of the metal ion content in the feed phase and phase receiver after the separation process was done by atomic absorption spectrometer.

Synthesis of Compounds Carrier TMEAA

Eugenoxi Acetic Acid Synthesis

A total of 5 g of eugenol was added to the boiling flask size of 100 ml, and then added a solution of 17.5 mL NaOH 33% (33 g NaOH in 100 mL) of. Subsequently the mixture was stirred for approximately for 30 minutes, and added 12.5 mL of a 50% solution of chloroacetic acid (50 g in 100 mL water) slowly with a pipette and stirred constantly. The mixture was heated in a water bath with a temperature of 80-90° C. Heating was carried out for 2 hours, then cooled and acidified with 6 M HCl until pH reached 1. Step further was extracted with diethylether for 3 times, each 50 mL. Ether extracts were combined and extracted with sodium bicarbonate 5% w / v for 3 times each 30 mL, and then the water layer was acidified with 6 M HCl to pH = 1. The subsequent steps were filtered, dried and weighted. The results were analyzed by FTIR and ^{1}H NMR.

Synthesis Thiazoethyle Methyl Eugenoxi Acetic Acid (TMEAA)

Amount of 3 g of eugenoxi acetic acid was added to three neck flask of 100 mL size with additional equipment (an addition funnel, reflux) and .added by 3 ml of thionyl chloride dropwise. Then the mixture was refluxed for 150 minutes in a warm water bath (40 ° C), and then allowed to cool. Subsequently added to the mixture was added 2.5 mL tiazoletanol dropwise and refluxed again in the warm water bath (40° C) for 6 hours. After coolled, the results obtained were dissolved in chloroform and washed with water. The extraction was dried with anhydrous sodium sulphate, filtered and then evaporated to remove the remaining solvent. The results obtained were analyzed by FTIR and ^{1}H NMR and also GC MS.

RESULTS AND DISCUSSION

This chapter describes the synthesis result TMEAA compounds and their use as a carrier in the recovery of metal compounds Cu^{2+}, Cd^{2+} and Cr^{3+} with techniques BLM (Bulk Liquid Membrane). TMEAA compound was synthesized from eugenol. Eugenol was converted into EOA, EOA was generated synthesized into TMEAA with the compound 4-methyl-5-thiazoetanol.

Synthesis Eugenoxi Acetic Acid (EAA)

Eugenoxi acetic acid synthesis was carried out by addition NaOH and chloroacetic acid. Hydroxy group in eugenol can react with NaOH to form salts eugenolat. This eugenolat salt are easy to be reacted with chloroacetic acid to form eugenoxi acetic acid. Eugenoxi acetic acid formation reaction can be shown in Fig 2.

Eugenoxi acetic acid formed was purified using diethyl ether in order to remove non - polar impurities and NaHCO3 to remove polar impurities. Eugenoxi acetic acid was pure white, insoluble in ether, methanol and chloroform. The yield was 77.4 %

Synthesis of Thiazoethyl Methyl Eugenoxi Acetic Acid (TMEAA)

TMEAA was synthesized from Eugenoxi acetic acid by addition thionyl chloride. Synthesis of TMEAA is an esterification reaction which are reversible so TMEAA should be made in hydrochloric acid form by addition thionyl chloride so that give yield above 80% [9]. Formation of TMEAA can be shown in Fig 3.

TMEAA was a liquid, viscous, blackish brown, fragrant, and gave a yield of 88%. This compound is soluble in benzene and chloroform, but insoluble in methanol. The results of the Analysis TMEAA using GC-MS can be seen in Fig 4 showed a single peak with a retention time of 26.512 minutes and the area of 100%. Peak in relative abundance (m / z) 347 is derived from the molecular ion TMEAA. Fragmentation patterns were formed from molecular ion peak TMEAA compounds as follows (Fig 5):

FTIR spectra TMEAA compounds can be seen in Fig 6 and Table 1. Absorption bands in the area of 3077.51 cm^{-1} was the range =C-H sp^2. Regional absorption band 1511.48 cm^{-1} indicates that the double bond was derived from the vibrations of the C=C aromatic core. This was supported by their absorption at 916.16 cm^{-1} region are showing their aromatic substituents. Sp^3 C-H bond absorption band appeared at 1416.28 cm^{-1} region. The infrared spectrum showed ester carbonyl group with the emergence of regional absorption at 1761.74

cm^{-1}. Based on the FTIR spectra of compounds TMEAA can be concluded that the wide band of hydroxyl group (OH) acids owing EOA at wave number around 3500 cm^{-1} [10] had not appeared again, this proves that it has been formed an ester.

Analysis of compounds by using ^{1}H NMR TMEAA can be seen in Fig 7. The differences were apparent in the spectra ^{1}H NMR spectra of TMEAA with eugenol [4] in which the appearance of a singlet peak at 8.68 ppm δ adsorbed by 1atom H of thiazole, absorption at δ 2.30 ppm (J) was an atomic absorption H at ($-CH_3-$), H atoms of ($-CH_2-$) indicated on the uptake of δ 3.98 ppm (H) and δ 4.96 ppm (F). So it can be concluded that the esterification reaction has occurred.

Based on the analysis of GC-MS, FTIR and NMR can be concluded that the compound TMEAA (thiazoethyl methyl eugenoxi acetic acid) has been formed by the relative purity of 100% and has a molecular weight relative 347 g / mol.

Transport Metals With BLM Technique

TMEAA was then used as a carrier to transport metal ionic with BLM technique. Transport metal ionic with BLM technique was done by fillling U tube (with a feed phase as much as 13 mL containing a mixture of 30 ppm respectively of Cu^{2+}, Cd^{2+} and Cr^{3+} with pH of 3.2. As the carrier used weight variation TMEAA monomer liquid membrane that was 0.7 grams; 0.5 grams; and 0.3 grams respectively in 30 ml of chloroform. While the stripping phase was used 13 mL HCl at pH variation (pH 1; pH 1.48 ~ 1.5; and pH 1.9). This system was stirred at a constant speed for 24 hours.

In the process of recovery of heavy metal with this BLM technique the changes of pH in the feed phase and the stripping phase was occured. This pH change indicates the exchange mechanism of metal and H^+ ions between the two phases. Mechanism of transport of metal ions from the feed phase to the stripping phase through the membrane as shown in Fig 8.

From Table 2 can be seen that the changes in pH after stirring for 24 hours. In feed phase was occured decreased pH, contrary with in stripping phase (increased pH). This is due to when the feed and the membrane phase were contact, carrier compounds will bind to metal ions to form complexes, this complex will further be brought into the interface membrane-stripping phase. In this interface, the carrier compound released metal ions and replaced with H +. This ion H + in the feed phase to be released and replaced with a metal ion. This process occurs repeatedly until no metal ions can be exchanged.

Transport Metals Using TMEAA

Recovery of heavy metal by TMEAA in this study was conducted by performing transport with different concentration of liquid membranes to determine the selectivity and effectiveness of TMEAA using techniques BLM. Results transport at pH 1.5 was shown in Fig 9. From Fig 9 showed that the sequence selectivity TMEAA compound was Cu^{2+}, Cd^{2+} and Cr^{3+} or borderline metals, soft and hard. This phenomena was due to TMEAA compound containing N and S groups, wherein N belonged to the borderline base that will form strong complexes with borderline acids (Cu^{2+}). While the S group belonged to the soft ones so that this base will form strong complexes with soft acids (Cd^{2+}). This was consistent with the theory HSAB (Hard Soft Acid Base) [2]. Transport results obtained can be seen that the metal Cu^{2+} transport have a greater percent as shown in the diagram above. This was due to the unsaturated nitrogen contained in TMEAA compound. The nitrogen atom will be double bonded to an metal atom that close to it. This double bonds participate in π bond with metal ions (Cu^{2+}) so that improve the stability of the complex [11] and Cu^{2+} transported more than Cd^{2+}, and Cr^{3+}. Mass changes on the carrier compounds can also affect the amount of metal transport. The results showed that the greater mass of the carrier compound, the more metal can be transported. For the transport heavy metal with pH variation shown in Fig 10.

To determine the effect of pH stripping phase to transport of metal ion with BLM techniques was conducted by varying the pH of HCl in the stripping phase. Seen in Fig 10 pH 1.5 Cu^{2+}, Cd^{2+}, and Cr^{3+} were transported large enough so that this pH can be used for the exploration. When we interest to make separation among of them we can use pH 1.9, because at that pH, Cu^{2+} was transported much otherwise Cd^{2+} and Cr^{3+}.

CONCLUSION

1. Thiazoethyl methyl eugenoxi acetic acid can be synthesized from eugenol and can be used as carrier compound in BLM technique.
2. Active groups N and S in TMEAA have selectivity to Cu^{2+} (borderline) and Cd^{2+} (soft).

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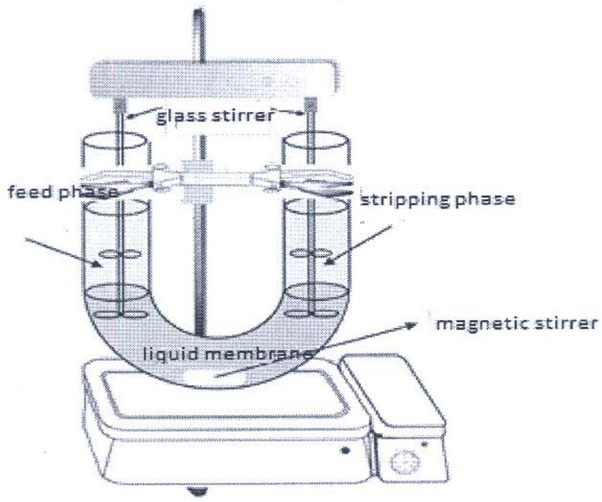

Fig 1. U Tube BLM

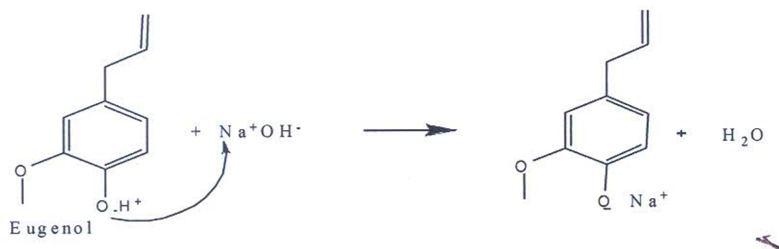

Fig 2. Reaction Formation of Eugenoxi Acetic Acid

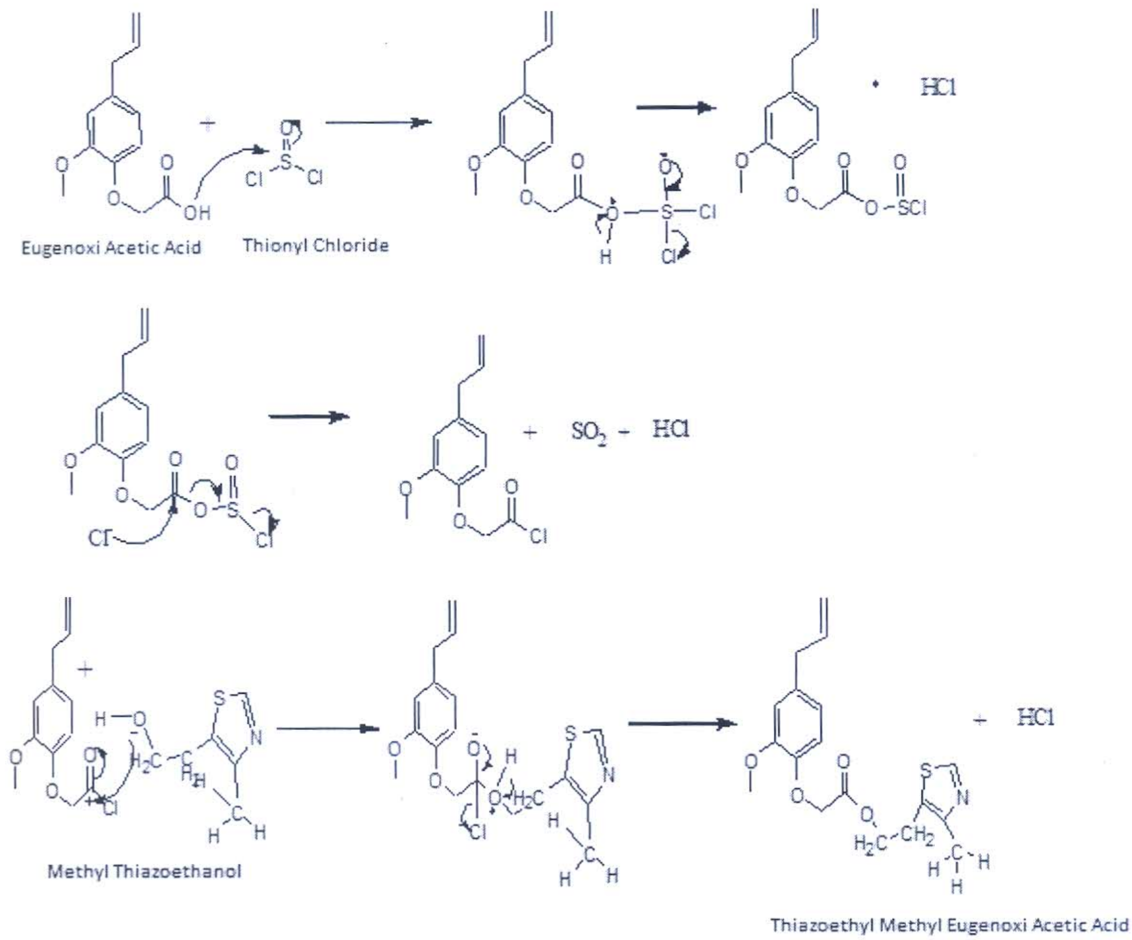

Fig 3. Reaction Formation of TMEAA

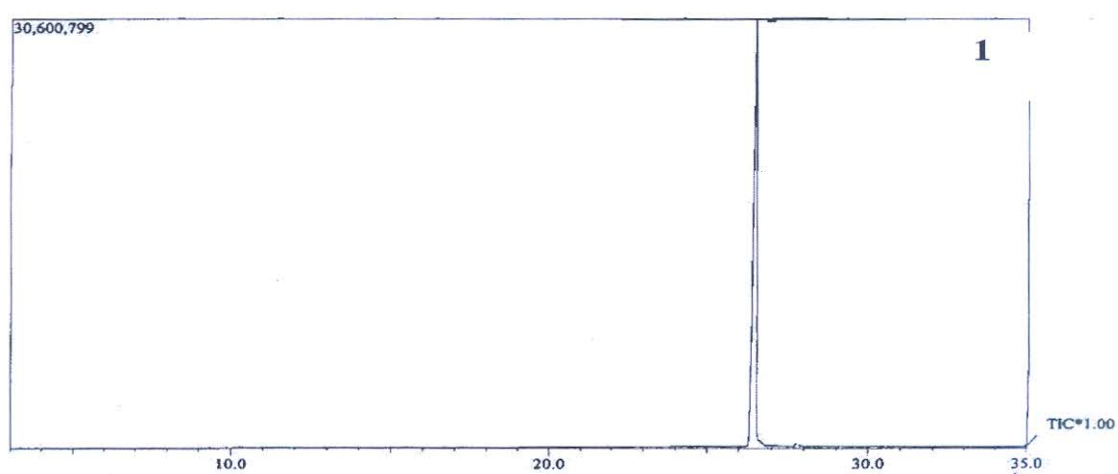

Fig 4. Gas chromatography TMEAA Compounds (1) and a mass spectrum of Compound TMEAA

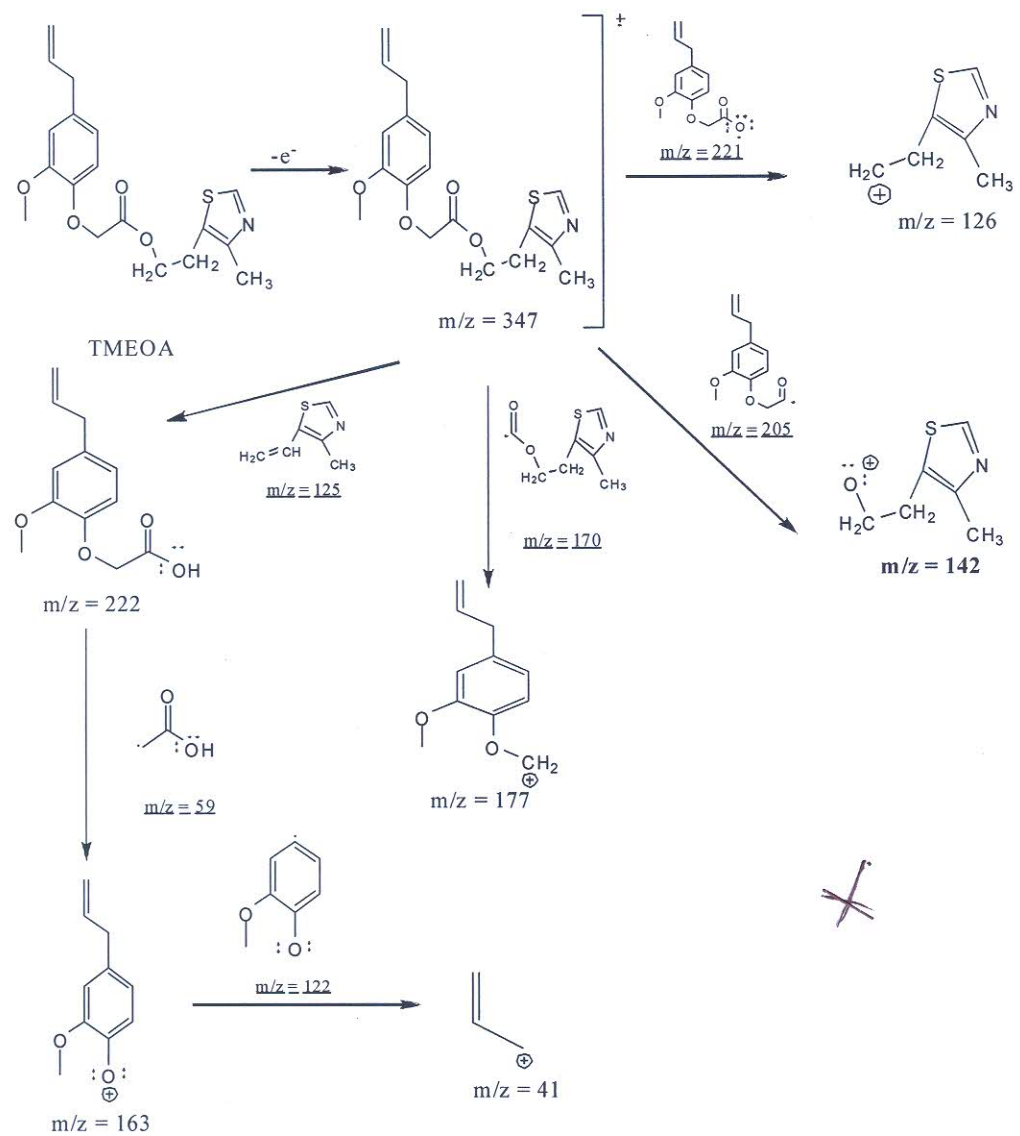

Fig 5. Fragmentation patterns of Compounds TMEAA

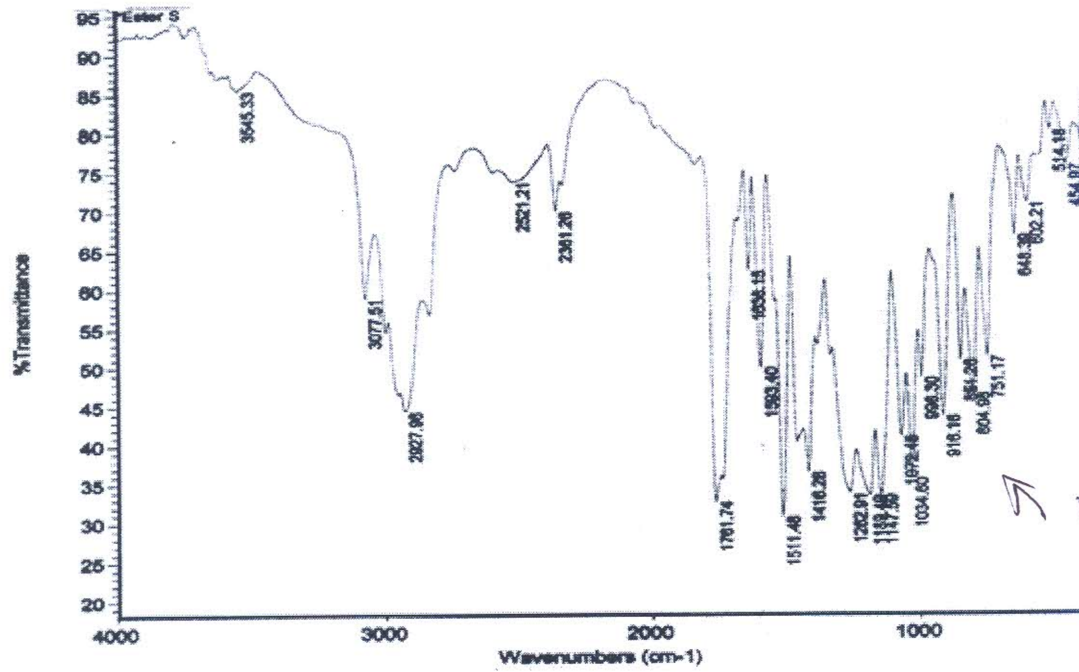

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Fig 6. FTIR spectra of compounds TMEAA

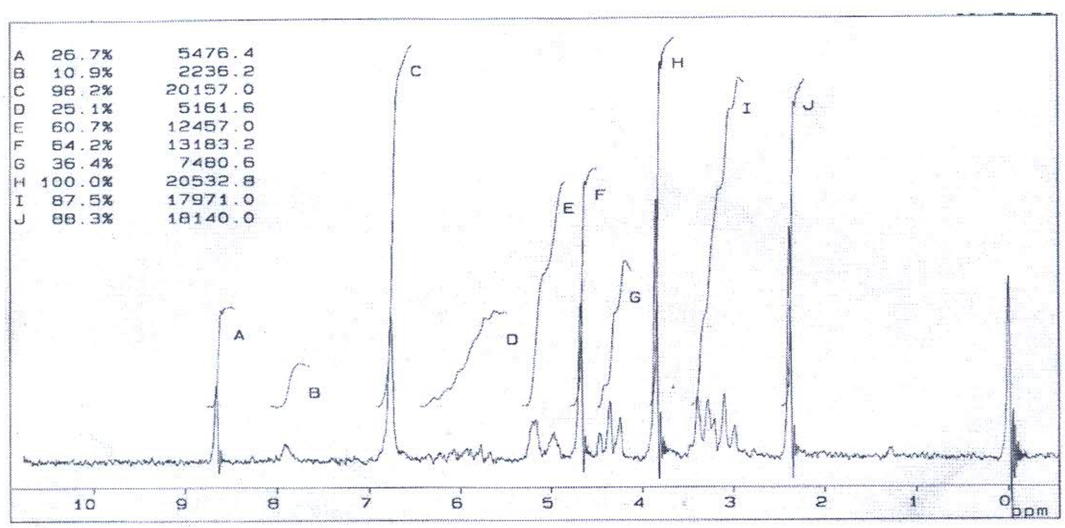

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Fig 7. ¹H NMR TMEAA

Fig 8. Cation Exchange Mechanism

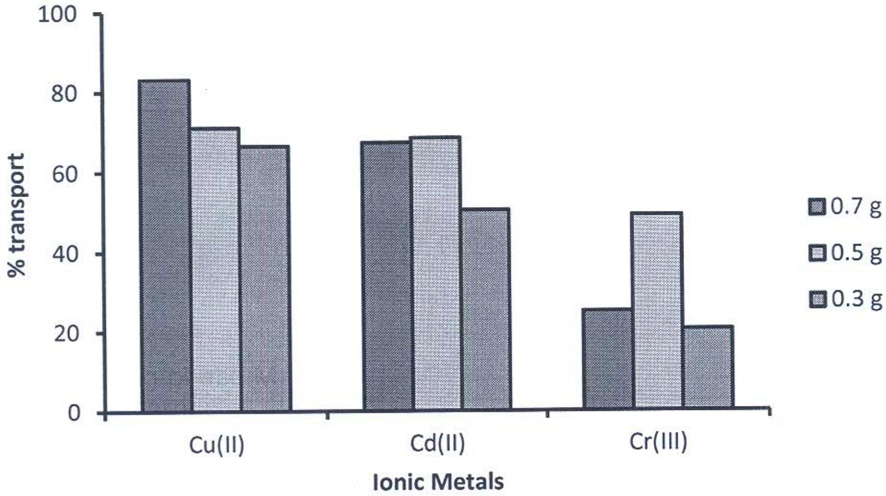

Fig 9. Heavy Metal Ion Transport Diagram In Stripping Phase.

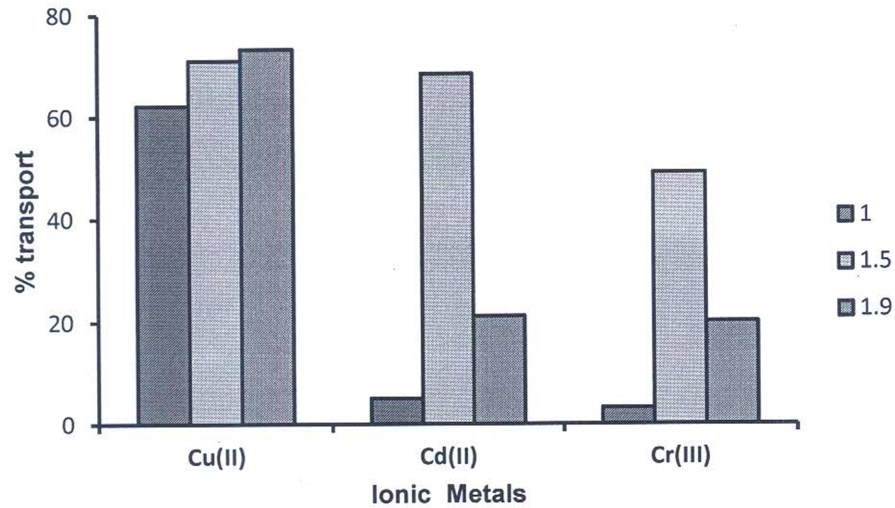

Fig 10. Transport Diagram Metal Variation pH

Table 1. Interpretaion of spectra of compounds TMEAA

Characteristic Groups	Bound Type	Absorption (cm^{-1})
Carbon Karbon unsaturated double bond	C_{sp2}-H (stretching)	3077.51
Aromatic	C=C (stretching)	1511.48
	C=C (bending)	916.16
Metilen (-CH_2-)	C_{sp3}-H (stretching)	1416.28
Carbonil	C=O (stretching)	1761.74
Ether	C-O (bending)	1262.91

Table 2. Changes in pH Measurement

pH	Membrane	pH Feed		pH Stripping	
		Initial	After 24 hs	Initial	After 24 hs
1	TMEAA-2	3,2	2,9	1	1,7
	TMEAA-1	3,2	2,9	1,5	2,7
1.5	TMEAA-2	3,2	2,2	1,5	1,6
	TMEAA-3	3,2	2,4	1,5	1,7
1.9	TMEAA-2	3,2	2,1	1,9	2,4

Information:
TMEAA-1: TMEAA with a mass of 0.7 g
TMEAA-2: TMEAA with a mass of 0.5 g
TMEAA-3: TMEAA with a mass of 0.3 g

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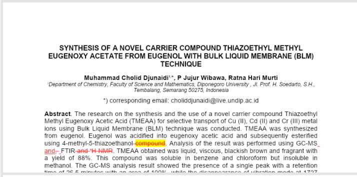

SYNTHESIS OF A NOVEL CARRIER COMPOUND THIAZOETHYL METHYL EUGENOXY ACETATE FROM EUGENOL WITH BULK LIQUID MEMBRANE (BLM) TECHNIQUE

Muhammad Cholid Djunaidi[1,*], P Jujur Wibawa, Ratna Hari Murti

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Abstract. The research on the synthesis and the use of a novel carrier compound Thiazoethyl Methyl Eugenoxy Acetic Acid (TMEAA) for selective transport of Cu (II), Cd (II) and Cr (III) metal ions using Bulk Liquid Membrane (BLM) technique was conducted. TMEAA was synthesized from eugenol. Eugenol was acidified into eugenoxy acetic acid and subsequently esterified using 4-methyl-5-thiazoethanol ~~compound~~. Analysis of the result was performed using GC-MS and FTIR ~~and ¹H NMR~~. TMEAA obtained was liquid, viscous, blackish brown and fragrant with a yield of 88%. This compound was soluble in benzene and chloroform but insoluble in methanol. The GC-MS analysis result showed the presence of a single peak with a retention

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#25075 Summary

SUMMARY REVIEW EDITING

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Title and Abstract

Title	Synthesis of A Novel Carrier Compound Thiazoethyl Methyl Eugenoxyacetate from Eugenol and Its Use in the Bulk Liquid Membrane Technique

Abstract *Research into the synthesis and use of a novel carrier compound, thiazoethyl methyl eugenoxyacetic acid (TMEAA) for selective transport of Cu(II), Cd(II) and Cr(III) metal ions in the bulk liquid membrane (BLM) technique was conducted. TMEAA was synthesized from eugenol. Eugenol was acidified into eugenoxyacetic*

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technique was conducted. TMEAA was synthesized from eugenol. Eugenol was acidified into eugenoxyacetic acid and subsequently esterified using 4-methyl-5-thiazoethanol. Analysis of the result was performed using GC-MS and FTIR. The TMEAA obtained was liquid, viscous, blackish-brown and fragrant, with a yield of 88%. This compound was soluble in benzene and chloroform but insoluble in methanol. The GC-MS analysis result showed the presence of a single peak, with a retention time of 26.5 min and an area of 100%, while the disappearance of vibration mode at 1727 cm^{-1} was attributed to acid absorption and the FTIR spectrum indicated that formation of an ester group had occurred. TMEAA was used as a carrier compound in the BLM technique to transport Cu(II), Cd(II) and Cr(III), using chloroform as a solvent. The results showed that TMEAA was more selective for Cu(II) and Cd(II) than Cr(III). Moreover, the research proved that N and S groups of TMEAA were selective for Cu (II) and Cd (II).

Indexing

Keywords Bulk Liquid Membrane (BLM); selective transport; thiazoethyl methyl eugenoxyacetic acid; eugenol

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Supporting Agencies

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#25075 Review

SUMMARY **REVIEW** EDITING

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Authors	Muhammad Cholid Djunaidi, Pratama Jujur Wibawa, Ratna Hari Murti
Title	Synthesis of A Novel Carrier Compound Thiazoethyl Methyl Eugenoxyacetate from Eugenol and Its Use in the Bulk Liquid Membrane Technique
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Editor	Dwi Siswanta

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CURRENT ISSUE

SYNTHESIS OF A NOVEL CARRIER THIAZOETHYL METHYL EUGENOXI ACETATE FROM EUGENOL WITH BULK LIQUID MEMBRANE (BLM) TECHNIQUE

Abstract. The research on the synthesis and using of a novel carrier Thiazoethyl Methyl Eugenoxy Acetic Acid (TMEAA) has conducted to selective transport metals of Cu (II), Cd (II) and Cr (III) with Bulk Liquid Membrane Technique (BLM). TMEAA was synthesized from eugenol. Eugenol was acidified into eugenoxy acetic acid and then followed by esterified using the 4-methyl-5-thiazoethanol compound. Analysis of the results was performed by GC-MS, FTIR and ^{1}H NMR. TMEAA that to obtained was liquid, viscous, blackish brown, fragrant with a yield of 88%. This compound was soluble in benzene and chloroform but insoluble in methanol. The results of the GC-MS analysis showed a single peak with a retention time of 26.5 minutes with an area of 100%, while the disappearance of the acid absorption of 1727 cm^{-1} in the FTIR spectra indicate that formation ester groups occurred. TMEAA was used as carrier technique BLM in chloroform to transport Cu (II), Cd (II) and Cr (III). The results showed that TMEAA was more selectivity toward Cu(II) and Cd(II) than Cr(III). The research proved that the group N and S of TMEAA selective for Cu (II) and Cd (II).

Comment [LK1]: This statement should be proved by conduction separation of metal ion by unmodified membrane

Keywords: BLM, selective transport, Thiazoethyl Methyl Eugenoxy Acetic Acid, eugenol.

Abstrak. Telah dilakukan penelitian tentang sintesis dan penggunaan Senyawa Carrier Tiazoetil Metil Eugenoksi Asetat untuk transpor selektif logam-logam Cu(II), Cd(II) dan Cr(III) menggunakan Teknik Membran Cair Ruah (BLM) dan menentukan selektifitas carrier tersebut. TMEAA disintesis dari eugenol menjadi asam eugenoksi asetat dilanjutkan dengan esterifikasi menggunakan senyawa 4-metil-5 tiazoetanol. Analisis hasil dilakukan dengan GC-MS, FTIR dan ^{1}H NMR. TMEAA yang diperoleh berbentuk cair, kental, berwarna coklat kehitaman, berbau harum dengan rendemen reaksi 88%. Senyawa ini larut dalam benzena dan kloroform, namun sukar larut dalam metanol. Hasil analisa GC-MS menunjukkan satu puncak dengan waktu retensi 26,5 menit dengan luas area 100%, sementara hilangnya serapan asam pada 1727 cm^{-1} pada spektra FTIR menunjukkan terbentuknya gugus ester. TMEOA hasil sintesis digunakan sebagai *carrier* teknik BLM dalam pelarut kloroform untuk transpor Cu (II), Cd (II) dan Cr (III). Hasil yang diperoleh TMEAA lebih selektif terhadap Cu (II) dan Cd (II) daripada Cr (III). Hasil penelitian membuktikan bahwa gugus N dan S dari TMEAA selektif terhadap Cu(II) dan Cd(II).
Kata Kunci: BLM, selective transport, Tiazoetil Metil Eugenoksi asetat, eugenol.

INTRODUCTION

Separation of heavy metals with the liquid membrane is one of the development solvent extraction method that can be used for the recovery of heavy metals from wastewater, valuable metal exploration from the mining of material and for the purpose of analysis. Advantages of liquid membrane system are selective and efficient, the little consumption of solvent, can be carried out continuously in a single unit operation, simple, and inexpensive [1], molecular diffusion in liquids is faster than in solids and therefore solid membranes with micron thickness cannot compete with liquid membranes with respect to the transfer intensity [2].

The stability of complex between metal and carrier compound determine the selectivity of separation using liquid membrane technique. The stability of the complex is determined by several factors, including the type of donor atoms (active group) owned carrier compound (ligand structure) that suitable with a metal electron configuration [3-7] and also pH of solutions [4-5]. The use of a carrier compound in liquid membrane techniques is to improve the efficiency and selectivity of transport [8].

Eugenol contained in clove oil has three active groups: allyl, methoxy, and hydroxyl. From the hydroxyl groups can be substituted by more selective groups. Make eugenol has potential as a selective compound carrier. Eugenol has been widely used for the separation of heavy metals, including eugenol polymer (poly eugenol) used to adsorb Fe (III) ion [9,10], as a functional polymer in the membrane in situ [11] and in particles membrane [12].

Eugenol derivatives with N-donor atoms from pyridyl carbinol were selective to borderline metal (Cu^{2+}) [13]. The working principle of the compound carrier is based by theory HSAB (grouping acid-base based on the hardness and softness) which states that, in general, ion hard metals (such as alkali metals, alkaline earth, and Cr^{3+}) form a stronger complex with donor atoms hardware (such as O) [14], ion soft metals (such as Cd^{2+}) with donor atoms of soft (such as S) [15] and metal ions borderline (such as Cu^{2+}) with donor atoms borderline (such as N) [13, 16-18]. A carrier compound that has active group nitrogen atom (N) and a sulfur atom (S) is expected to selective to Cu^{2+} and Cd^{2+}.

In this research we will recover metal ions Cr^{3+}, Cd^{2+} and Cu^{2+} from a waste simulation using Thiazoethyl Methyl Eugenoxy Acetic Acid that synthesized from eugenol using Bulk Liquid Membrane BLM (Bulk Liquid Membrane) techniques. BLM is a simple of the liquid membrane and usually used for the study in the liquid membrane transport processes.

EXPERIMENTAL SECTION

Materials.

The materials were purchased from SIGMA-Aldrich, Eugenol, BF_3-diethylether while other reagents were purchased from E Merck, Germany: $SOCl_2$, 4-methyl-5-thiazoleethanol, NaOH, chloroacetic acid, $CrCl_3$. $6H_2O$, $CuCl_2.2H_2O$, $CdCl_2.H_2O$. Chloroform, Methanol, Diethyl ether and demineralized water were purchased from Bratachem.

Comment [LK2]: Other information such as molecular weight, purity and so on should be provided

Instrumentation

The instruments used to characterization of TMEAA in this study were FTIR Spectrophotometer (Shimadzu 8201PC), and GC-MS (Shimadzu QP2010S), NMR ^{1}H JEOL-MY60, analytical balance (Mettler Toledo AB54-S), Atomic Absorption Spectrophotometer (Perkin-Elmer), pH meter (HACH E C20).

Equipment: Laboratory Glassware and a set of tools BLM (U tube, Fig 1).

Procedure

Liquid Membrane Preparation

0.7 g thiazoethyl methyl eugenoxy acetic acid (TMEAA) was dissolved in 30 mL of chloroform.

Recovery process

A solution of 30 mL TMEAA was poured in the U-tube was placed between the feed phase and phase receiver each 13 mL, then stirred for 24 hours.

Measurement of pH

After the feed phase and stripping phase through the mixing process for 24 hours, the pH was measured by pH meter on both sides.

Analysis by AAS

Analysis of the metal ion content in the feed phase and phase receiver after the separation process was done by atomic absorption spectrometer.

Synthesis of Compounds Carrier TMEAA

Eugenoxy Acetic Acid Synthesis

A total of 5 g of eugenol was added to the boiling flask size of 100 ml, and then added a solution of 17.5 mL NaOH 33% (33 g NaOH in 100 mL) of. Subsequently, the mixture was stirred for approximately for 30 minutes, and added 12.5 mL of a 50% solution of chloroacetic acid (50 g in 100 mL water) slowly with a pipette and stirred constantly. The mixture was heated in a water bath to a temperature of 80-90 °C. Heating was carried out for 2 hours, then cooled and acidified with 6 M HCl until pH reached 1. A step further was extracted with diethyl ether for 3 times, each 50 mL. Ether extracts were combined and extracted with sodium bicarbonate 5% w / v for 3 times each 30 mL, and then the water layer was acidified with 6 M HCl to pH = 1. The subsequent steps were filtered, dried and weighed. The results were analyzed by FTIR and ^{1}H NMR.

Comment [LK3]: Can not be found in Materials section

Comment [LK4]: Can not be found in materials section

Synthesis Thiazoethyle Methyl Eugenoxy Acetic Acid (TMEAA)

The amount of 3 g of eugenoxy acetic acid was added to three neck flask of 100 mL size with additional equipment (an addition funnel, reflux) and .added by 3 ml of thionyl chloride dropwise. Then the mixture was refluxed for 150 minutes in a warm water bath (40 ° C), and then allowed to cool. Subsequently added to the mixture was added 2.5 mL tiazoletanol dropwise and refluxed again in the warm water bath (40° C) for 6 hours. After cooled, the results obtained were dissolved in chloroform and washed with water. The extraction was dried over anhydrous sodium sulfate, filtered and then evaporated to remove the remaining solvent. The results obtained were analyzed by FTIR and ^{1}H NMR and also GC-MS.

Comment [LK5]: Can not be found in material section

Comment [LK6]: This section need to be re-arranged in appropriate order such as: 1. Preparation of EAA, preparation of TMEAA, separation of metal ion by TMEAA and so on..

RESULTS AND DISCUSSION

This chapter describes the synthesis result TMEAA compounds and their use as a carrier in the recovery of metal compounds Cu^{2+}, Cd^{2+} and Cr^{3+} with techniques BLM (Bulk Liquid Membrane). TMEAA compound was synthesized from eugenol. Eugenol was converted into EOA, EOA was generated synthesized into TMEAA with the compound 4-methyl-5-thiazoetanol.

Comment [LK7]: ?

Synthesis Eugenoxy Acetic Acid (EAA)

Eugenoxy acetic acid synthesis was carried out by addition NaOH and chloroacetic acid. Hydroxy group in eugenol can react with NaOH to form salts eugenolate. This eugenolate salt was easy to be reacted with chloroacetic acid to form eugenoxy acetic acid.

Eugenoxy acetic acid formed was purified using diethyl ether in order to remove non-polar impurities and $NaHCO_3$ to remove polar impurities. Eugenoxy acetic acid was pure white, insoluble in ether, methanol, and chloroform. The yield was 77.4 %

Synthesis of Thiazoethyl Methyl Eugenoxy Acetic Acid (TMEAA)

TMEAA was synthesized from Eugenoxy acetic acid by addition thionyl chloride. Synthesis of TMEAA is an esterification reaction which are reversible so TMEAA should be made in hydrochloric acid form by addition thionyl chloride so that give yield above 80% [19].

TMEAA was a liquid, viscous, blackish brown, fragrant, and gave a yield of 88%. This compound is soluble in benzene and chloroform but insoluble in methanol. The results of the Analysis TMEAA using GC-MS can be seen in Fig 2 showed a single peak with a retention time of 26.512 minutes and the area of 100%. Peak in relative abundance (m / z) 347 is derived from the molecular ion TMEAA.

FTIR spectra TMEAA compounds can be seen in Fig 3. Absorption bands in the area of 3077 cm^{-1} were the range =C-H sp^2. Regional absorption band 1511 cm^{-1} indicates that the double bond was derived from the vibrations of the C=C aromatic core. This was supported by their absorption at 916 cm^{-1} regions are showing their aromatic substituents. Sp^3 C-H bond absorption band appeared at 1416 cm^{-1} region. The infrared spectrum showed ester carbonyl group with the emergence of regional absorption at 1761 cm^{-1}. Based on the FTIR spectra of compounds TMEAA can be concluded that the wide band of hydroxyl group (OH) acids owing EOA at wave number around 3500 cm^{-1} [10] had not appeared again, this proves that it has been formed an ester.

Analysis of compounds by using ^1H NMR TMEAA can be seen in Fig 7. The differences were apparent in the spectra ^1H NMR spectra of TMEAA with eugenol [10] in which the appearance of a singlet peak at 8.68 ppm δ adsorbed by 1atom H of thiazole, absorption at δ 2.30 ppm (J) was an atomic absorption H at ($-CH_3-$), H atoms of ($-CH_2-$) indicated on the uptake of δ 3.98 ppm (H) and δ 4.96 ppm (F). So it can be concluded that the esterification reaction has occurred.

Based on the analysis of GC-MS, FTIR and NMR can be concluded that the compound TMEAA (thiazoethyl methyl eugenoxy acetic acid) has been formed by the relative purity of 100% and has a molecular weight relative 347 g / mol.

Transport Metals with BLM Technique

TMEAA was then used as a carrier to transport metal ionic with BLM technique. Transport metal ionic with BLM technique was done by filling U-tube (with a feed phase as much as 13 mL containing a mixture of 30 ppm respectively of Cu^{2+}, Cd^{2+} and Cr^{3+} with pH of 3.2. As the carrier used weight variation TMEAA monomer liquid membrane that was 0.7 grams; 0.5 grams; and 0.3 grams respectively in 30 ml of chloroform. While the stripping phase was used 13 mL HCl at pH variation (pH 1; pH 1.48 ~ 1.5; and pH 1.9). This system was stirred at a constant speed for 24 hours.

Comment [LK8]: It would be better to move this paragraph to procedure section

In the process of recovery of heavy metal with this BLM technique, the changes of pH in the feed phase and the stripping phase occurred. This pH change indicates the exchange mechanism of metal and H^+ ions between the two phases. Mechanism of transport of metal ions from the feed phase to the stripping phase through the membrane as shown in Fig 5 and pH changed can be shown in Table 1.

From Table 1 can be seen that the changes in pH after stirring for 24 hours. In feed phase was occurred decreased pH, contrary within stripping phase (increased pH). This is due to when the feed and the membrane phase were contacted, carrier compounds will bind to metal ions to form complexes, this complex will further be brought into the interface membrane-stripping phase. In this interface, the carrier compound released metal ions and replaced with H^{+}. This ion H^{+} in the feed phase to be released and replaced with a metal ion. This process occurs repeatedly until no metal ions can be exchanged.

Transport Metals Using TMEAA

Recovery of heavy metal by TMEAA in this study was conducted by performing transport with different concentration of liquid membranes to determine the selectivity and effectiveness of TMEAA using techniques BLM. Results transport at pH 1.5 was shown in Fig 6. From Fig 6 showed that the sequence selectivity TMEAA compound was Cu^{2+}, $Cd^{2+,}$ and Cr^{3+} or borderline metals, soft and hard. This phenomenon was due to TMEAA compound containing N and S groups, wherein N belonged to the borderline base that will form strong complexes with borderline acids (Cu^{2+}). While the S group belonged to the soft ones so that this base will form strong complexes with soft acids (Cd^{2+}). This was consistent with the theory HSAB (Hard Soft Acid Base) [3]. Transport results obtained can be seen that the metal Cu^{2+} transport have a greater percent as shown in Fig 9. This was due to the unsaturated nitrogen contained in TMEAA compound. The nitrogen atom will be double bonded to a metal atom that closes to it. These double bonds participate in π bond with metal ions (Cu^{2+}) so that improve the stability of the complex [20] and Cu^{2+} transported more than Cd^{2+} and Cr^{3+}. Mass changes on the carrier compounds can also affect the amount of metal transport [4]. The results showed that the greater mass of the carrier compound, the more metal can be transported. For the transport heavy metal with pH variation shown in Fig 7.

Comment [LK9]: Additional schematic picture of interaction between metal ion with TMEAA is needed

To determine the effect of pH stripping phase to transport of metal ion with BLM techniques was conducted by varying the pH of HCl in the stripping phase. It can be seen in Fig 7 pH 1.5 Cu^{2+}, Cd^{2+}, and Cr^{3+} were transported large enough so that this pH can be used for the exploration. When we interest to make separation among of them we can use pH 1, because, at that pH, $Cu2^{+}$ was transported much otherwise Cd^{2+} and Cr^{3+}. Selectivity coefficient Cu(II)/Cd(II) and Cu(II)/Cr(III) for BLMs decrease with an HCl concentration increase in the stripping phase The same tendency was reported in the literature [6,21].

CONCLUSION

In the present study, Thiazoethyl methyl eugenoxy acetic acid can be synthesized from eugenol and can be used as carrier compound in BLM technique. Active groups N and S in TMEAA have selectivity to Cu^{2+} (borderline) and Cd^{2+} (soft).

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Comment [LK10]: Please be consistent on writing reference

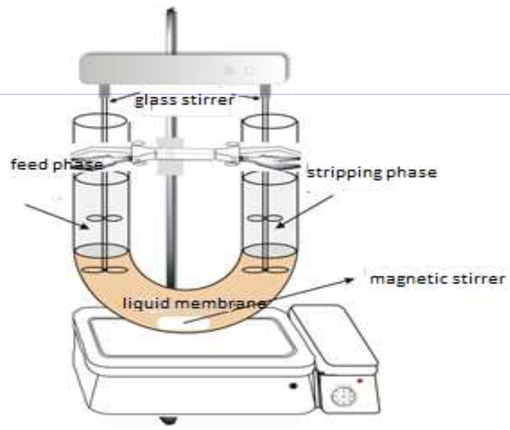


Fig 1. U Tube BLM

Comment [LK11]: This picture is perfectly same with that in article: doi:10.1088/1757-899X/172/1/012032

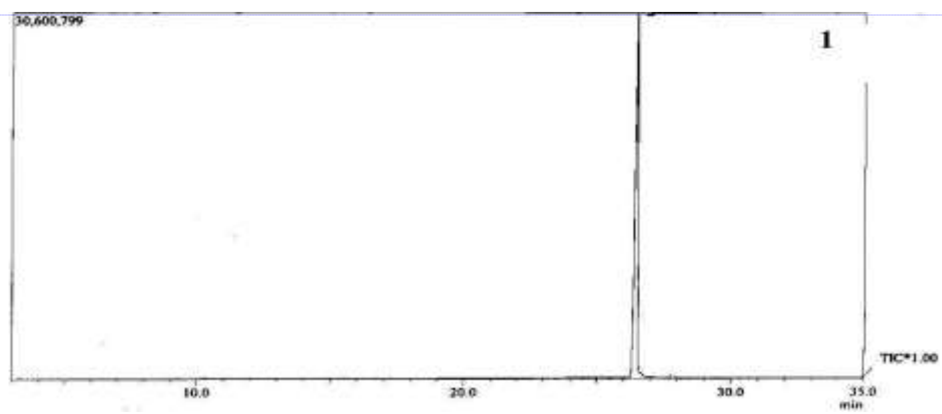


Fig 2. Gas chromatography TMEAA Compounds (1) and a mass spectrum of Compound TMEAA

Comment [LK12]: X and Y axes should be added

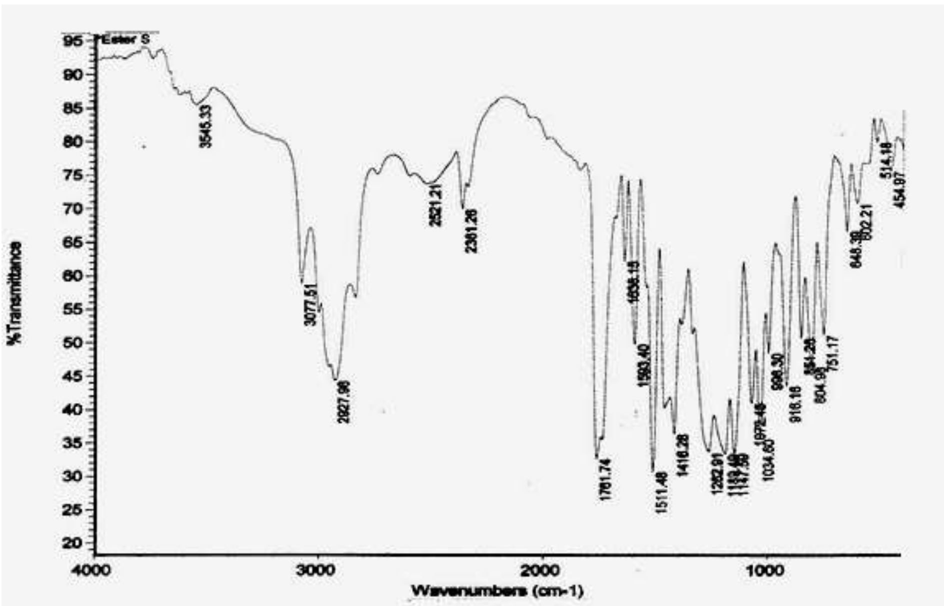


Fig 3. FTIR spectra of compounds TMEAA

Comment [LK13]: This picture is not clear

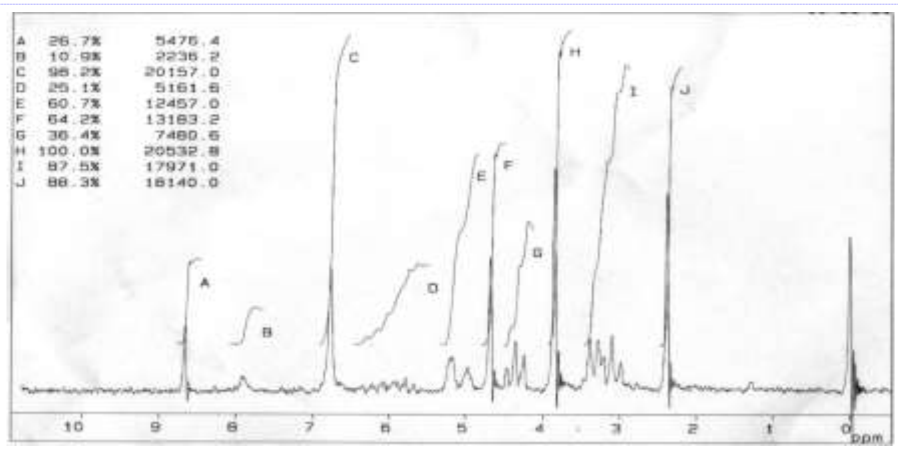
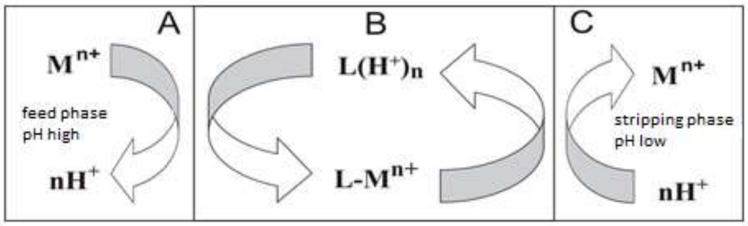


Fig 4. ^{1}H NMR TMEAA

Comment [LK14]: This data is perfectly same with that in article: doi:10.1088/1757-899X/172/1/012032 which refers to polyeugenoksi acetic acid instead of TMEAA

Comment [LK15]: Mechanism described in Fig 5 cannot be used to describe metal separation by TMEAA since TMEAA contain S group which follows complexation mechanism instead of ion exchange mechanism



A: feed phase C: stripping phase M: metal
B: the organic phase L: carrier

Fig 5. Cation Exchange Mechanism

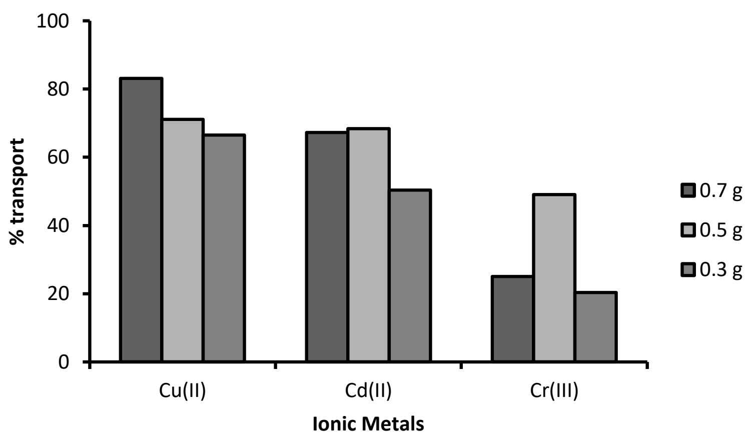


Fig 6. Heavy Metal Ion Transport Diagram In Stripping Phase.

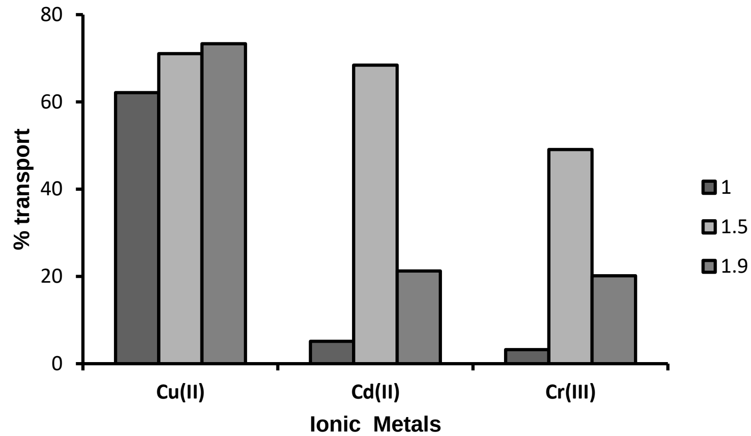


Fig 7. Transport Ion Metal Diagram at Variation pH in Stripping Phase

Table 1. Changes in pH Measurement

pH	Membrane	pH Feed		pH Stripping	
		Initial	After 24 h	Initial	After 24 h
1	TMEAA-2	3.2	2.9	1	1.7
	TMEAA-1	3.2	2.9	1.5	2.7
1.5	TMEAA-2	3.2	2.2	1.5	1.6
	TMEAA-3	3.2	2.4	1.5	1.7
1.9	TMEAA-2	3.2	2.1	1.9	2.4

Information:

TMEAA-1: TMEAA with a mass of 0.7 g
TMEAA-2: TMEAA with a mass of 0.5 g
TMEAA-3: TMEAA with a mass of 0.3 g

Comment [LK16]: Based on Fig 5, lower pH will give a higher %transport. For Cu(II), why did % transport increase by increasing of pH?

SYNTHESIS OF A NOVEL CARRIER COMPOUND THIAZOETHYL METHYL EUGENOXY ACETATE FROM EUGENOL WITH BULK LIQUID MEMBRANE (BLM) TECHNIQUE

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Abstract. The research on the synthesis and the use of a novel carrier compound Thiazoethyl Methyl Eugenoxy Acetic Acid (TMEAA) for selective transport of Cu (II), Cd (II) and Cr (III) metal ions using Bulk Liquid Membrane (BLM) technique was conducted. TMEAA was synthesized from eugenol. Eugenol was acidified into eugenoxy acetic acid and subsequently esterified using 4-methyl-5-thiazoethanol compound. Analysis of the result was performed using GC-MS, FTIR and ^{1}H NMR. TMEAA obtained was liquid, viscous, blackish brown and fragrant with a yield of 88%. This compound was soluble in benzene and chloroform but insoluble in methanol. The GC-MS analysis result showed the presence of a single peak with a retention time of 26.5 minutes with an area of 100%, while the disappearance of vibration mode at 1727 cm^{-1} attributed to acid absorption in the FTIR spectrum indicated that formation of ester group occurred. TMEAA was used as a carrier compound in BLM technique to transport Cu (II), Cd (II) and Cr (III) using chloroform as a solvent. The results showed that TMEAA was more selective to Cu(II) and Cd(II) than Cr(III). Moreover, the research proved that N and S groups of TMEAA were selective to Cu (II) and Cd (II).

Comment [LK1]: This statement should be proved by conducting separation experiment of metal ion by unmodified membrane

Keywords: BLM, selective transport, Thiazoethyl Methyl Eugenoxy Acetic Acid, eugenol.

Abstrak. Telah dilakukan penelitian tentang sintesis dan penggunaan Senyawa Carrier Tiazoetil Metil Eugenoksi Asetat untuk transpor selektif logam-logam Cu(II), Cd(II) dan Cr(III) menggunakan Teknik Membran Cair Ruah (BLM) dan menentukan selektifitas carrier tersebut. TMEAA disintesis dari eugenol menjadi asam eugenoksi asetat dilanjutkan dengan esterifikasi menggunakan senyawa 4-metil-5 tiazoetanol. Analisis hasil dilakukan dengan GC-MS, FTIR dan ^{1}H NMR. TMEAA yang diperoleh berbentuk cair, kental, berwarna coklat kehitaman, berbau harum dengan rendemen reaksi 88%. Senyawa ini larut dalam benzena dan kloroform, namun sukar larut dalam metanol. Hasil analisa GC-MS menunjukkan satu puncak dengan waktu retensi 26,5 menit dengan luas area 100%, sementara hilangnya serapan asam pada 1727 cm^{-1} pada spektra FTIR menunjukkan terbentuknya gugus ester. TMEOA hasil sintesis digunakan sebagai *carrier* teknik BLM dalam pelarut kloroform untuk transpor Cu (II), Cd (II) dan Cr (III). Hasil yang diperoleh TMEAA lebih selektif terhadap Cu (II) dan Cd (II) daripada Cr (III). Hasil penelitian membuktikan bahwa gugus N dan S dari TMEAA selektif terhadap Cu(II) dan Cd(II).
Kata Kunci: BLM, selective transport, Tiazoetil Metil Eugenoksi asetat, eugenol.

INTRODUCTION

Separation of heavy metals with the liquid membrane is one of the development solvent extraction methods that can be used for the recovery of heavy metals from wastewater and valuable metal exploration from the mining of material. Moreover, it can also be used for the analysis purposes. The advantages of liquid membrane system are selective and efficient, low solvent consumption, simple, inexpensive and can be carried out continuously in a single unit operation [1]. In addition, molecular diffusion in liquids is faster than in solids. Therefore, solid membranes with micron thickness cannot compete with liquid membranes with respect to the transfer intensity [2].

The stability of complex between metal and carrier compound determines the selectivity of separation using liquid membrane technique. The stability of the complex is determined by several factors, including the type of donor atoms (active group) contained in carrier compound (ligand structure) suitable for a metal electron configuration [3-7] and also pH of solutions [4-5]. The use of a carrier compound in liquid membrane techniques is to improve the efficiency and selectivity of transport [8].

Eugenol contained in clove oil has three active groups: allyl, methoxy and hydroxy. The hydroxyl groups that can be substituted by more selective groups lead to eugenol is potential for a selective carrier compound.

Eugenol has been widely used for the separation of heavy metals, including eugenol polymer (poly eugenol) used to adsorb Fe (III) ion [9,10], as a functional polymer in in-situ formation of the membrane [11] and in membrane particles [12].

Eugenol derivatives with N-donor atoms from pyridyl carbinols are selective to borderline metal (Cu^{2+}) [13]. The working principle of the compound carrier is based on theory of HSAB (grouping acid-base based on the hardness and softness) which states that, in general, hard metal ions (such as alkali metals, alkaline earth, and Cr^{3+}) form a stronger complex with hard donor atoms (such as O) [14], soft metal ions (such as Cd^{2+}) with soft donor atoms (such as S) [15] and the borderline metal ions (such as Cu^{2+}) with the borderline donor atoms (such as N) [13, 16-18]. A carrier compound that has nitrogen (N) and sulfur (S) active groups are expected to be selective to Cu^{2+} and Cd^{2+}.

In this research we will recover Cr^{3+}, Cd^{2+} and Cu^{2+} metal ions from the waste model using Thiazoethyl Methyl Eugenoxy Acetic Acid (TMEAA) synthesized from eugenol using Bulk

Liquid Membrane BLM (Bulk Liquid Membrane) technique. BLM is a simple liquid membrane and usually used for the study of the liquid membrane transport processes.

EXPERIMENTAL SECTION

Materials

Materials were used in this research were eugenol, BF_3-diethylether (purchased from SIGMA-Aldrich), $SOCl_2$, 4-methyl-5-thiazoleethanol, NaOH, chloroacetic acid, $CrCl_3.6H_2O$ $CuCl_2.2H_2O$, $CdCl_2.H_2O$ (purchased from Merck, Germany). Other reagents including chloroform, methanol, diethyl ether and demineralized water were purchased from Bratachem.

Comment [LK2]: Please write all chemical with more detail information including it's purity

Instrumentations

The instruments used to characterize TMEAA in this study were FTIR Spectrophotometer (Shimadzu 8201PC), GC-MS (Shimadzu QP2010S), NMR ^{1}H JEOL-MY60, analytical balance (Mettler Toledo AB54-S), AAS (Perkin Elmer), pH meter (HACH E C20).

Equipment: Laboratory Glassware and a set of BLM tools (U tube, Fig 1).

Procedures

Comment [LK3]: Procedure section need to be rearrange in appropriate order such as: 1. Preparation of EAA, preparation of TMEAA, separation experiment….

Liquid Membrane Preparation

0.7 g thiazoethyl methyl eugenoxy acetic acid (TMEAA) was dissolved in 30 mL chloroform.

Recovery process

30 mL TMEAA was poured into the U-tube and was placed between the feed and receiver phases and then stirred for 24 hours. The volume of each phase was 13 mL.

Measurement of pH

After stirring for 24 hours, pH of both feed and receiver phases was measured using pH meter.

Analysis by AAS

Analysis of the metal ions content in the feed and receiver phases after the separation process was carried out using atomic absorption spectrometer.

Synthesis of Compounds Carrier TMEAA

Synthesis of Eugenoxy Acetic Acid

5 g eugenol was added into a round-bottom 100-mL boiling flask. After that 17.5 mL NaOH 33% was added and subsequently, the mixture was stirred for approximately 30 minutes. The next step was adding 12.5 mL of 50% chloroacetic acid slowly with a pipette and the mixture was stirred constantly. The mixture had been heated in a water bath with a temperature of 80-90 °C for 2 hours, then was cooled and acidified using 6 M HCl until the pH reached 1. A further step was the extraction of the mixture using 50 mL of diethyl ether for 3 times. This extraction resulted in ether extracts. The ether extracts were then combined and re-extracted with 30 mL sodium bicarbonate 5% w/v for 3 times. This extraction process produced two layers, namely, water and ether layers. The water layer was then acidified using concentrated HCl 6 M to reach pH 1. The final steps respectively were filtering, drying and weighing. The results were analyzed by FTIR and ^{1}H NMR.

Comment [LK4]: Not mentioned in materials section

Comment [LK5]: Not mentioned in materials section

Comment [LK6]: Not mentioned in materials section

Synthesis Thiazoethyle Methyl Eugenoxi Acetic Acid (TMEAA)

3 g of eugenoxy acetic acid was added into a reflux apparatus. After that, 3 mL of thionyl chloride was added into it dropwise. Then the mixture was refluxed for 150 minutes in a water bath with the temperature 40 °C and allowed to cool at room temperature after reaching the time. The next step was adding 2.5 mL of thiazolethanol dropwise and refluxing again in the warm-water bath (40 °C) for 6 hours. After cooling, the result obtained was then extracted using chloroform and then washed with water. The extract was dried over anhydrous sodium sulfate, filtered and then evaporated to remove the remaining solvent. The result obtained was analyzed using FTIR, ^{1}H NMR and GC-MS.

Comment [LK7]: Not mentioned in materials section

RESULTS AND DISCUSSION

This chapter describes the synthesis of TMEAA compound and its use as a carrier in the recovery of Cu^{2+}, Cd^{2+} and Cr^{3+} metal ions using Bulk Liquid Membrane (BLM) technique. TMEAA compound was synthesized from eugenol. Eugenol was converted into EOA, EOA was then converted into TMEAA by esterification reaction with the compound 4-methyl-5-thiazoetanol.

Synthesis Eugenoxi Acetic Acid (EAA)

The eugenoxy acetic acid synthesis was carried out by the addition of NaOH and chloroacetic acid. Hydroxy group in eugenol can react with NaOH to form a eugenolat salt. This eugenolat salt is easy to be reacted with chloroacetic acid to form eugenoxy acetic acid.

The eugenoxy acetic acid formed was purified using diethyl ether in order to remove non -polar impurities and using $NaHCO_3$ to remove polar impurities. Eugenoxy acetic acid was pure white and insoluble in ether, methanol, and chloroform. The yield was 77.4 %.

Synthesis of Thiazoethyl Methyl Eugenoxy Acetic Acid (TMEAA)

TMEAA was synthesized from the eugenoxy acetic acid by addition of thionyl chloride. Synthesis of TMEAA is an esterification reaction which is reversible so TMEAA should be conducted in hydrochloric acid form by addition of thionyl chloride so that results in yield above 80% [19].

TMEAA was a liquid, viscous, blackish brown, fragrant, and gave a yield of 88%. This compound was soluble in benzene and chloroform but insoluble in methanol. The analysis of TMEAA using GC-MS can be seen in Fig. 2 which showed a single peak with a retention time of 26.512 minutes and the area of 100%. Peak in relative abundance (m / z) 347 is derived from the molecular ion of TMEAA.

FTIR spectrum of TMEAA compound is presented in Fig 3. The absorption band in the area of 3077 cm^{-1} is attributed to =C-H sp^2. The regional absorption band at 1511 cm^{-1} indicates the presence of the vibrations of the C=C aromatic core supported by the absorption at 916 cm^{-1} regions showing the aromatic substituents. Sp^3 C-H bond absorption band appears at 1416 cm^{-1} region. The vibration mode emerges at 1761 cm^{-1} indicates the existence of ester carbonyl group. Based on the FTIR spectrum of TMEAA compound, the wide band at wavenumber around 3500 cm^{-1} attributed to a hydroxyl group (OH) which belongs to EOA [10] disappears, this proves that it has been formed an ester.

Analysis of TMEAA compound using ^1H NMR is shown in Fig 7. The difference between TMEAA and eugenol is apparent in the spectrum of ^1H NMR [10] in which the appearance of a singlet peak at δ 8.68 ppm adsorbed by 1 atom H of thiazole, absorption at δ 2.30 ppm (J) is an atomic absorption of hydrogen atoms coming from methyl ($-CH_3-$); meanwhile, the atomic absorption of hydrogen atoms attributed to allyl ($-CH_2-$) is indicated by the uptake of δ 3.98 ppm (H) and δ 4.96 ppm (F). So it can be concluded that the esterification reaction has occurred.

Based on the analysis of GC-MS, FTIR, and NMR, it can be concluded that the TMEAA compound (thiazoethyl methyl eugenoxy acetic acid) was formed by the relative purity of 100% and a relative molecular weight of 347 g / mol.

Transport Metals using BLM Technique

TMEAA was then used as a carrier compound to transport metal ions using BLM technique. Metal ions transport using BLM technique was done by filling U-tube (with a feed phase containing 13 mL of a mixture consisting of 30 ppm Cu^{2+}, Cd^{2+} and Cr^{3+} with pH of 3.2). As the carrier compound, the weight of TMEAA was varied, namely, 0.7; 0.5; and 0.3 g and then poured into 30 ml chloroform for each weight. In the meantime, the stripping phase contained 13 mL HCl at pH variation (pH 1; pH 1.48 ~ 1.5; and pH 1.9). This system had been stirred at a constant speed for 24 hours.

Comment [LK8]: Should be put in procedure section

In the process of recovery of heavy metals using this BLM technique, the changes of pH both in the feed and the stripping phases occurred. This pH changes indicated the exchange mechanism of metal and H^+ ions between the two phases. Mechanism of metal ions transport from the feed phase to the stripping phase through the membrane is shown in Fig 5 and the pH changes is presented in Table 1.

From Table 1, it can be seen that the changes in pH after stirring for 24 hours. In feed phase pH decreased, in contrast, the pH increased in stripping phase. This is due to when the feed and the membrane phase were in contact, carrier compounds bound to metal ions to form complexes, further, these complexes were brought into the interface of membrane-stripping phase. In this interface, the carrier compounds released metal ions and replaced them with H^+. Ion H^+ in the feed phase was released and replaced with a metal ion. This process occurs repeatedly until no metal ions were exchanged.

Metals Transport using TMEAA

Recovery of heavy metals by TMEAA in this study was conducted by performing transport with different concentration of liquid membranes to determine the selectivity and effectiveness of TMEAA using BLM technique. The result of metal transport at pH 1.5 is shown in Fig 6. Fig 6 showed that the sequence selectivity of TMEAA compound was Cu^{2+}, $Cd^{2+,}$ and Cr^{3+} or borderline, soft and hard metals, respectively. This phenomenon occurred because TMEAA compound contains N and S groups, in which N belongs to the borderline bases will form strong complexes with borderline acids (Cu^{2+}). While the S group belongs to the soft one so that this base will form strong complexes with soft acids (Cd^{2+}). This was consistent with the theory of Hard Soft Acid Base (HSAB) [3]. Based on the transport results obtained as shown in Fig. 9, it can be seen that the transport of Cu^{2+} metal ion showed the greatest percentage. This was due to the unsaturated nitrogen contained in TMEAA compound. The nitrogen atom bond a metal atom that closes to it in a double bond. This double bond participated in π bond with metal ions (Cu^{2+}) so that improve the stability of the complex [20] and Cu^{2+} transported is higher than Cd^{2+} and Cr^{3+}. The polymer of TMAA was used by Djunaidi, et al, 2017 (21) for the same goal and found the similar sequence was Cd> Cu >> Cr.

Comment [LK9]: Schematic picture of interaction mechanism between metal ion and TMEAA need to be added on this manuscript so then this explanation will be easier to be understood

Mass of the carrier compounds used can also affect the amount of metal transport [4]. The result showed that the greater the mass of the carrier compound used, the more metal that can be transported. The transport of heavy metals with pH variation is shown in Fig 7.

Determination of the effect of pH in stripping phase for metal ions transport using BLM technique was conducted by varying the pH of HCl in the stripping phase. It can be seen in Fig 7 that at pH 1.5 Cu^{2+}, Cd^{2+}, and Cr^{3+} were transported large enough so that this pH condition can be used for the exploration. When we were interested in separation among them we used pH 1, because at pH 1, Cu^{2+} was transported greater than Cd^{2+} and Cr^{3+}. Selectivity coefficients of Cu(II)/Cd(II) and Cu(II)/Cr(III) for BLMs decreased with increasing HCl concentration in the stripping phase. The same tendency was reported in the literature [6, 22].

CONCLUSION

In the present study, thiazoethyl methyl eugenoxy acetic acid can be synthesized from eugenol and can be used as the carrier compound in BLM technique. The N and S active groups in TMEAA have selectivity to the Cu^{2+} (borderline) and Cd^{2+} (soft) metal ions.

Comment [LK10]: This statement is weak since there are no data about separation of metal ion by unmodified membrane (membrane without N and S)

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14. Djunaidi, M.C., Lusiana, R.A., Wibowa, P.J., Siswanta, D., and Jumina, 2007, *Alchemy*, 6, 40–49
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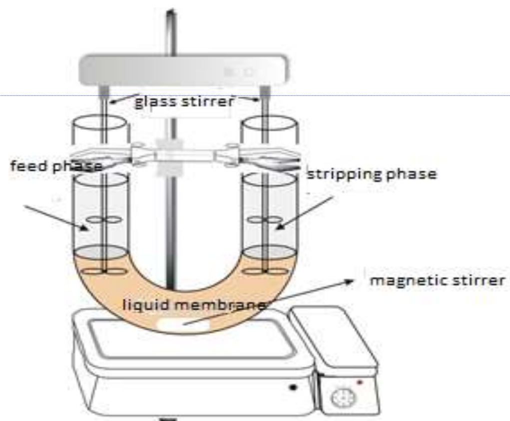


Fig 1. U Tube BLM

Comment [LK15]: This picture is perfectly same with that in article: doi:10.1088/1757-899X/172/1/012032 (Ref #21)

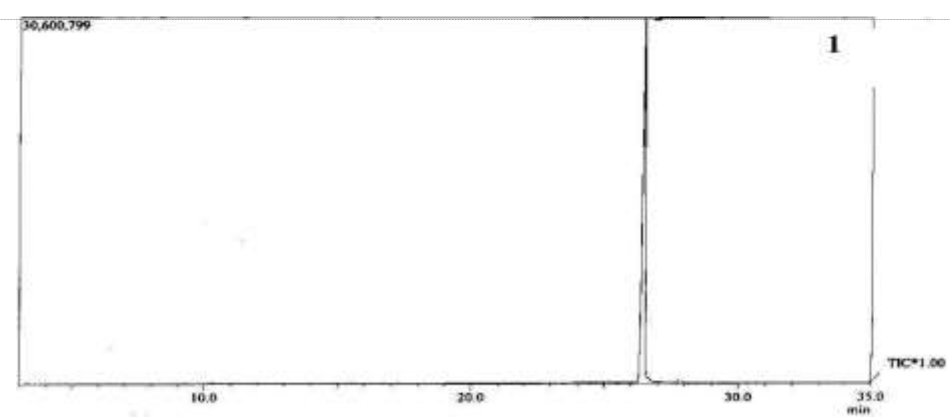


Fig 2. Gas chromatograph of TMEAA Compound

Comment [LK16]: X and Y axes should be written

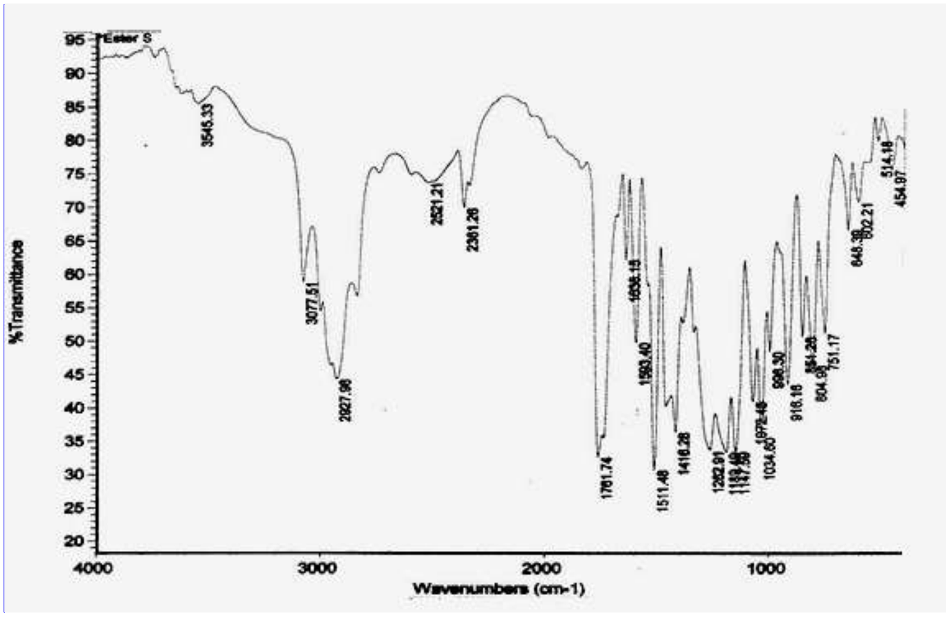


Fig 3. FTIR spectrum of TMEAA Compound

Comment [LK17]: This picture is not clear

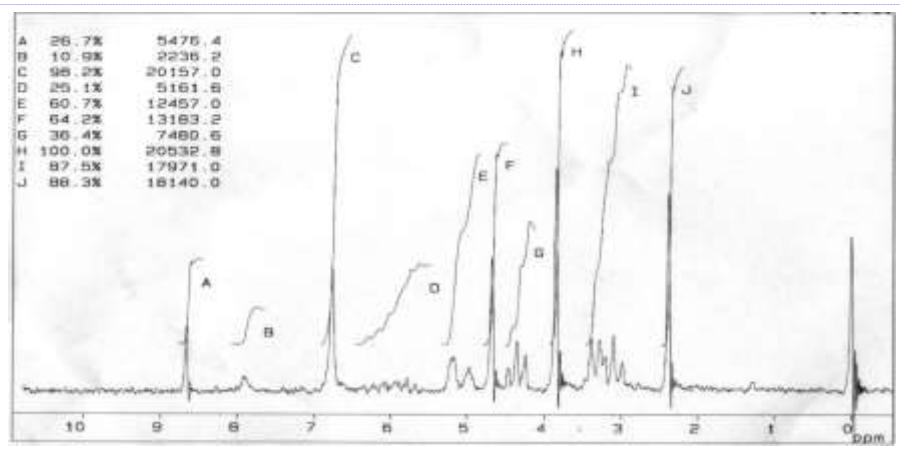
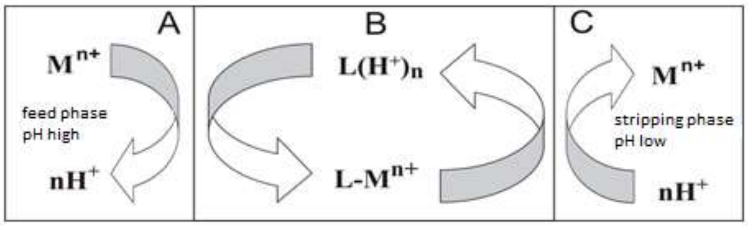


Fig 4. ^{1}H NMR spectrum of TMEAA

Comment [LK18]: This 1H-NMR is perfectly same with that in article: doi:10.1088/1757-899X/172/1/012032 which refers to polyeugenoksi acetic acid instead of TMEAA (Ref#21)



Comment [LK19]: This mechanism probably could be applied for N contained membrane. However for S contained membrane the mechanism is complexation rather than ion exchange

A: feed phase C: stripping phase M: metal
B: the organic phase L: carrier

Fig 5. Cation Exchange Mechanism

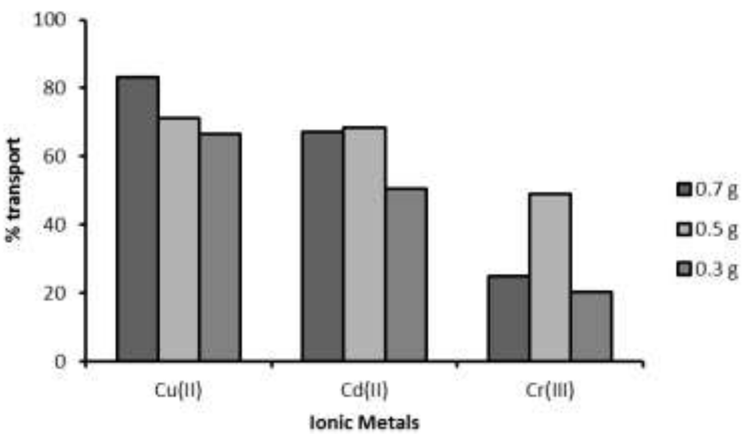
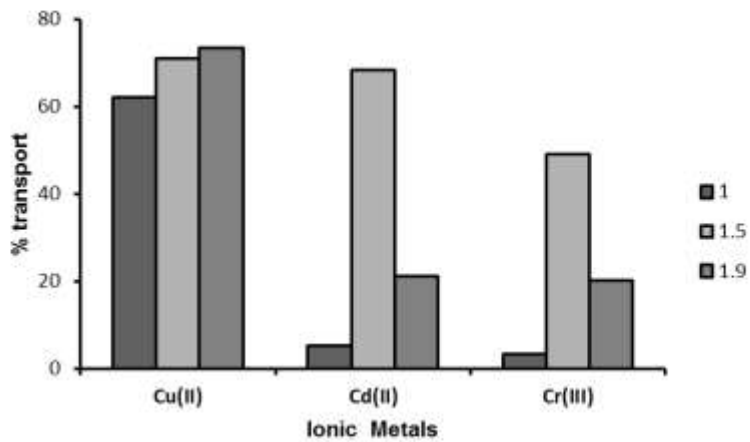


Fig 6. Diagram of Heavy Metal Ions Transport in Stripping Phase



Comment [LK20]: If the mechanism is like what have been described in Fig 5. Then why for transport of Cu(II) increase by increasing pH?. Lower pH should be more effective based on Fig 5

Fig 7. Diagram of Metal IonsTransport at Variation of pH in Stripping Phase

Table 1. Measurement of Changes in pH

pH	Membrane	pH Feed		pH Stripping	
		Initial	After 24 h	Initial	After 24 h
1	TMEAA-2	3.2	2.9	1	1.7
	TMEAA-1	3.2	2.9	1.5	2.7
1.5	TMEAA-2	3.2	2.2	1.5	1.6
	TMEAA-3	3.2	2.4	1.5	1.7
1.9	TMEAA-2	3.2	2.1	1.9	2.4

Information:

TMEAA-1: TMEAA with a mass of 0.7 g
TMEAA-2: TMEAA with a mass of 0.5 g
TMEAA-3: TMEAA with a mass of 0.3 g

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Synthesis of A Novel Carrier Compound Thiazoethyl Methyl Eugenoxyacetate from Eugenol and Its Use in the Bulk Liquid Membrane Technique

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ABSTRACT

Research into the synthesis and use of a novel carrier compound, thiazoethyl methyl eugenoxyacetic acid (TMEAA) for selective transport of Cu(II), Cd(II) and Cr(III) metal ions in the bulk liquid membrane (BLM) technique was conducted. TMEAA was synthesized from eugenol by acidification into eugenoxyacetic acid and subsequently esterified using 4-methyl-5-thiazoethanol. Analysis of the result was performed using GC-MS and FTIR. The TMEAA obtained was liquid, viscous, blackish-brown and fragrant, with a yield of 88%. This compound was soluble in benzene and chloroform but insoluble in methanol. The GC-MS analysis showed the presence of a single peak, with a retention time of 26.5 min, while the disappearance of vibration mode at 1727 cm^{-1} was attributed to acid absorption and the FTIR spectrum indicated that formation of an ester group had occurred. TMEAA was used as a carrier compound in the BLM technique to transport Cu(II), Cd(II) and Cr(III), using chloroform as a solvent. The results showed that TMEAA was more selective for Cu(II) and Cd(II) than Cr(III). Moreover, the research proved that N and S groups of TMEAA were selective for Cu (II) and Cd (II).

Keywords: *Bulk Liquid Membrane* (*BLM); selective transport; thiazoethyl methyl eugenoxyacetic acid; eugenol*

ABSTRAK

Telah dilakukan penelitian tentang sintesis dan penggunaan senyawa carrier tiazoetil metil eugenoksi asetat untuk transpor selektif logam-logam Cu(II), Cd(II) dan Cr(III) menggunakan Teknik Membran Cair Ruah (BLM). TMEAA disintesis dari eugenol menjadi asam eugenoksi asetat dilanjutkan dengan esterifikasi menggunakan senyawa 4-metil-5 tiazoetanol. Analisis hasil dilakukan dengan GC-MS dan FTIR. TMEAA yang diperoleh berbentuk cair, kental, berwarna coklat kehitaman, berbau harum dengan rendemen 88%. Senyawa ini larut dalam benzena dan kloroform, namun sukar larut dalam metanol. Hasil analisa GC-MS menunjukkan satu puncak dengan waktu retensi 26,5 menit, sementara hilangnya serapan asam pada 1727 cm^{-1} pada spektra FTIR menunjukkan terbentuknya gugus ester. TMEOA hasil sintesis digunakan sebagai carrier teknik BLM dalam pelarut kloroform untuk transpor Cu(II), Cd(II) dan Cr(III). Hasil yang diperoleh TMEAA lebih selektif terhadap Cu(II) dan Cd(II) daripada Cr(III). Hasil penelitian membuktikan bahwa gugus N dan S dari TMEAA selektif terhadap Cu(II) dan Cd(II).

Kata Kunci: *membran cair ruah; transport selektif; tiazoetil metil eugenoksi asetat; eugenol*

INTRODUCTION

Separation of heavy metals using liquid membranes is a solvent extraction method developed for use in the recovery of heavy metals from wastewater and for the extraction of valuable metals in the mining of materials. It can also be used for analysis purposes. The advantages of liquid membrane systems are that they are selective and efficient, involve low solvent consumption, are simple and inexpensive, and can be carried out continuously in a single unit operation [1]. In addition, molecular diffusion in liquids is faster than in solids, and so solid membranes with micron thicknesses cannot compete with liquid membranes in terms of transfer intensity [2].

The stability of the complex between the metal and the carrier compound determines the selectivity of separation in liquid membrane techniques. The stability of the complex is determined by several factors, including the type of donor atoms (active group) contained in the carrier compound (ligand structure), suitability for a metal electron configuration [3-7], and the pH of solutions [4-5]. The use of a carrier compound in liquid membrane techniques improves the efficiency and selectivity of transport [8].

Eugenol contained in clove oil has three active groups: allyl, methoxy and hydroxy. The hydroxyl group, which can be substituted by a more selective group, leads to eugenol being a potential selective carrier compound. Eugenol has been widely used for

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the separation of heavy metals, including eugenol polymer (polyeugenol) used to adsorb Fe(III) ions [9-10], as a functional polymer in in-situ formations of membranes [11] and in membrane particles [12].

Eugenol derivatives with N-donor atoms from pyridyl carbinols are selective for borderline metals (Cu^{2+}) [13]. The working principle of the compound carrier is based on HSAB theory (grouping acids and bases based on their hardness and softness) which states that, in general, hard metal ions (such as alkali metals, alkaline earths, and Cr^{3+}) form a stronger complex with hard donor atoms (such as O) [14], soft metal ions (such as Cd^{2+}) with soft donor atoms (such as S) [15] and borderline metal ions (such as Cu^{2+}) with borderline donor atoms (such as N) [13,16-18]. A carrier compound that has nitrogen (N) and sulfur (S) active groups is expected to be selective for Cu^{2+} and Cd^{2+}.

In this research, Cr^{3+}, Cd^{2+} and Cu^{2+} metal ions will be recovered from a waste model using thiazoethyl methyl eugenoxyacetic acid (TMEAA) synthesized from eugenol, using the BLM technique. A BLM is a simple liquid membrane used for the study of liquid membrane transport processes.

EXPERIMENTAL SECTION

Materials

The materials used in this research were eugenol p.a (SIGMA-Aldrich), BF_3-diethylether p.a. (SIGMA-Aldrich), $SOCl_2$ p.a (Merck), 4-methyl-5-thiazoleethanol p.a (Merck), NaOH p.a, (Merck), chloroacetic acid p.a (Merck), $CrCl_3.6H_2O$ p.a (Merck), $CuCl_2.2H_2O$ p.a (Merck), $CdCl_2.H_2O$ p.a (Merck), HCl p.a (Merck), sodium bicarbonate p.a. (Merck), sodium sulfate anhydrate p.a. (Merck). Other reagents, including chloroform, methanol, diethyl ether and demineralized water, were purchased from Bratachem.

Instrumentation

The instruments used to characterize TMEAA in this study were FTIR Spectrophotometer (Shimadzu 8201PC), GC-MS (Shimadzu QP2010S), analytical balance (Mettler Toledo AB54-S), AAS (Perkin Elmer), pH meter (HACH E C20). A set of BLM tools (U-tube) was used for transport study.

Procedure

Synthesis of compound carrier TMEAA

Synthesis of eugenoxyacetic acid (EOA). Eugenol (5 g) was placed in a round-bottomed 100 mL boiling flask. 17.5 mL NaOH 33% was added and the mixture was then stirred for approximately 30 min. Then 12.5 mL of 50% chloroacetic acid was slowly added with a pipette and the mixture was stirred constantly. The mixture was heated in a water bath with a temperature of 80–90 °C for 2 h, and was then cooled and acidified using 6 M HCl until the pH reached 1. The next step was the extraction of the mixture three times using 50 mL of diethyl ether, resulting in ether extracts. The ether extracts were then combined and re-extracted three times using 30 mL sodium bicarbonate 5% w/v. This extraction process produced water and ether layers. The water layer was then acidified using concentrated HCl 6 M to achieve pH 1. The final steps respectively were filtering, drying and weighing. The results were analyzed by FTIR.

Synthesis of TMEAA. Eugenoxyacetic acid (3 g) was placed in a reflux apparatus and 3 mL of thionyl chloride was added dropwise. The mixture was refluxed for 150 min in a water bath with a temperature of 40 °C and then allowed to cool at room temperature. In the next step 2.5 mL of thiazolethanol was adding dropwise and refluxed again in the water bath at 40 °C for 6 h. After cooling, the result obtained was extracted using chloroform and then washed with water. The extract was dried over anhydrous sodium sulfate, filtered, and then evaporated to remove remaining solvent. The result obtained was analyzed using FTIR and GC-MS.

Separation experiment

Transport of metals using the BLM technique. TMEAA (0.7 g) was dissolved in 30 mL chloroform and was then used as a carrier compound to transport metal ions using the BLM technique. Metal ion transport using the BLM technique was carried out by filling a u-tube with a feed phase containing 13 mL of a mixture consisting of 30 ppm Cu^{2+}, Cd^{2+} and Cr^{3+} with pH of 3.2. The TMEAA carrier compound in weights 0.7, 0.5, and 0.3 g was then poured into 30 mL chloroform for each weight. In the meantime, the stripping phase contained 13 mL HCl at a variety of pHs (pH 1, 1.48–1.5, and 1.9). These systems were then stirred at a constant speed for 24 h. After stirring for 24 h, pH of both feed and receiver phases was measured using a pH meter. Analysis of the metal ion content in the feed and receiver phases after the separation process was carried out using an atomic absorption spectrometer.

RESULT AND DISCUSSION

This chapter describes the synthesis of TMEAA and its use as a carrier in the recovery of Cu^{2+}, Cd^{2+}, and Cr^{3+} metal ions using the BLM technique. TMEAA compound was synthesized from eugenol. Eugenol was converted into EOA, which was then converted into

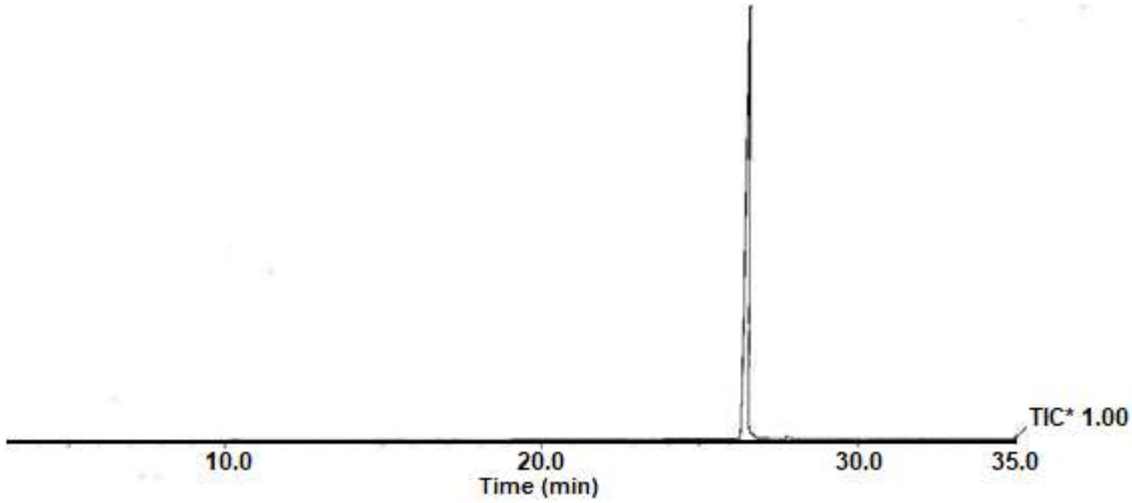


Fig 1. Gas chromatograph of TMEAA

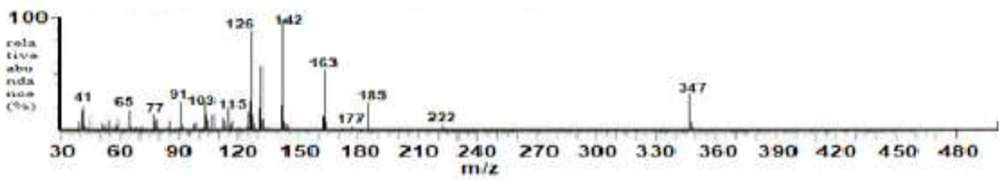


Fig 2. Spectrum mass of TMEAA

TMEAA by an esterification reaction with 4-methyl-5-thiazoetanol.

Synthesis of Eugenoxyacetic Acid

The eugenoxyacetic acid synthesis was carried out by the addition of NaOH and chloroacetic acid. The hydroxy group in eugenol can react with NaOH to form a eugenolate salt. This eugenolate salt reacts easily with chloroacetic acid to form eugenoxyacetic acid.

The eugenoxyacetic acid formed was purified using diethyl ether in order to remove non-polar impurities and $NaHCO_3$ to remove polar impurities. The eugenoxyacetic acid produced was a pure white substance, insoluble in ether, methanol, and chloroform. The yield was 77.4%.

Synthesis of TMEAA

TMEAA was synthesized from the eugenoxyacetic acid by the addition of thionyl chloride. Synthesis of TMEAA is an esterification reaction which is reversible, so TMEAA should be conducted in hydrochloric acid formed by the addition of thionyl chloride so that results yield above 80% [19].

The TMEAA produced was a liquid, viscous, blackish-brown, fragrant substance, and gave a yield of 88%. This compound was soluble in benzene and chloroform but insoluble in methanol. The analysis of TMEAA using GC-MS can be seen in Fig. 1, which shows a single peak with a retention time of 26.5 min. Peak in relative abundance (m/z) of 347 and the spectrum mass of fragmentation (Fig. 2) were suitable.

The FTIR spectrum of TMEAA compound is presented in Fig. 3. The absorption band in the area of 3077 cm^{-1} is attributed to =C-H sp^2. The absorption band at 1511 cm^{-1} indicates the presence of vibrations of the C=C aromatic core, and this is supported by the absorption at 916 cm^{-1} region showing the aromatic substituents. The sp^3 C-H bond absorption band appears at the 1416 cm^{-1} region. The vibration mode emerges at 1761 cm^{-1} indicating the existence of an ester carbonyl group. Based on the FTIR spectrum of the TMEAA compound, the wide band at wavenumber of 3888 and 3388 cm^{-1} is attributed to a hydroxyl group (OH) which belongs to EOA [10] disappearing, proving that an ester has been formed.

Based on the analysis by GC-MS and FTIR, it can be concluded that the TMEAA was formed with high purity and molecular weight of 347 g/mol.

In the process of recovery of heavy metals using this BLM technique, changes of pH both in the feed and the stripping phases occurred. These pH changes indicated the exchange mechanism of metal and H^+ ions between the two phases. The mechanism of metal ion transport from the feed phase to the stripping phase

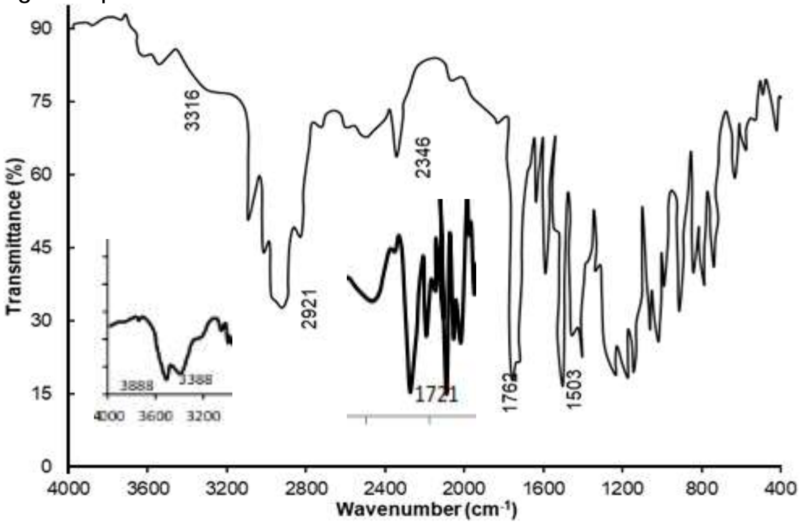
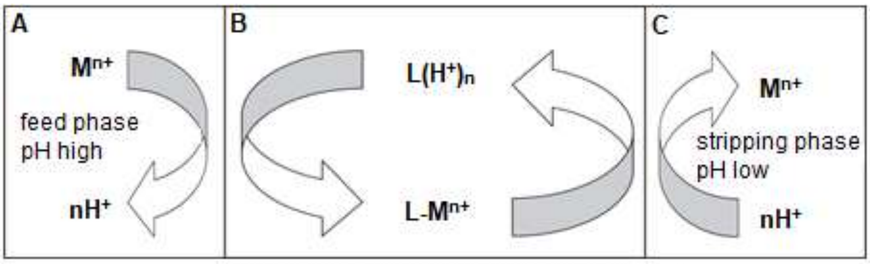


Fig 3. FTIR spectrum of TMEAA, insert FTIR spectrum of EOA



Legend: A: feed phase, B: organic phase, C: stripping phase, M: metal, L: carrier

Fig 4. Cation exchange mechanism

Table 1. Measurement of changes in pH

pH	Membrane	pH feed		pH stripping	
		Initial	After 24 h	Initial	After 24 h
1	TMEAA-2	3.2	2.9	1	1.7
	TMEAA-1	3.2	2.9	1.5	2.7
1.5	TMEAA-2	3.2	2.2	1.5	1.6
	TMEAA-3	3.2	2.4	1.5	1.7
1.9	TMEAA-2	3.2	2.1	1.9	2.4

Legend:
TMEAA-1: TMEAA with a mass of 0.7 g
TMEAA-2: TMEAA with a mass of 0.5 g
TMEAA-3: TMEAA with a mass of 0.3 g

through the membrane is shown in Fig. 4 and the pH changes are presented in Table 1.

In Table 1 the changes in pH after stirring for 24 h can be seen. In the feed phase pH decreased, in contrast, the pH increased in the stripping phase. This resulted from the feed and the membrane phase contact, in which carrier compounds bound to metal ions to form complexes and these complexes were then brought to the interface of the membrane-stripping phase. At this interface, the carrier compounds released metal ions and replaced them with H^+. An H^+ ion in the feed phase was released and replaced with a metal ion. This process occured repeatedly until no further metal ions were exchanged.

Metals Transport Using TMEAA

Recovery of heavy metals by TMEAA in this study was conducted by performing transport with different

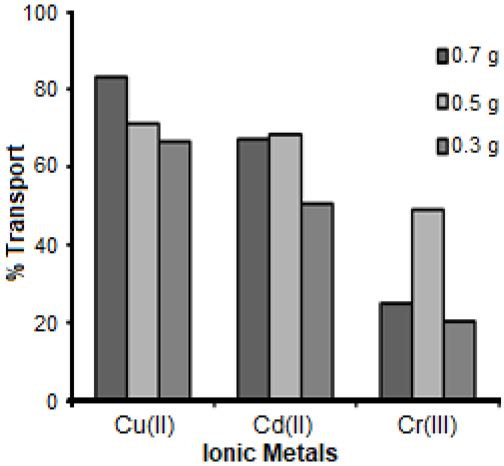


Fig 5. Heavy metal ion transport in stripping phase

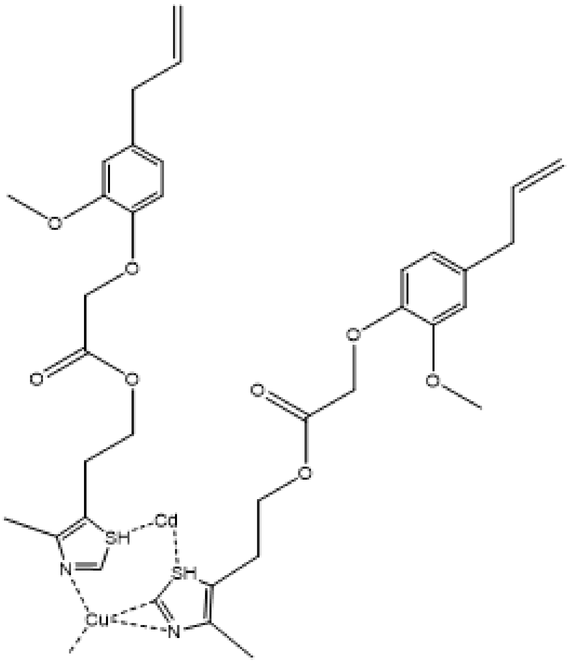


Fig 6. Interaction proposed between metal ions and TMEAA

concentration of liquid membranes to determine the selectivity and effectiveness of TMEAA used in the BLM technique. The result of metal transport at pH 1.5 is shown in Fig. 5, which shows that the sequence of selectivity of TMEAA was Cu^{2+}, Cd^{2+}, and Cr^{3+}, or borderline, soft, and hard metals, respectively. This phenomenon occurred because TMEAA contains N and S groups. N belongs to the borderline bases and will form strong complexes with borderline acids (Cu^{2+}), while the S group belongs to the soft category and so will form strong complexes with soft acids (Cd^{2+}). This was consistent with HSAB theory [3]. Based on the transport results obtained, as shown in Fig. 6, it can be seen that

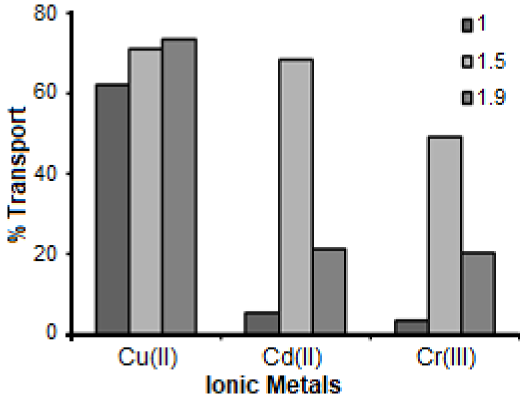


Fig 7. Ionic Metal transport at variations of pH in stripping phase

the transport of Cu^{2+} metal ions showed the greatest percentage. This was due to the unsaturated nitrogen contained in TMEAA. The nitrogen atom bonds with a metal atom closing it in a double bond. This double bond participated in π bonds with metal ions (Cu^{2+}) improving the stability of the complex [20] and so the amount of Cu^{2+} transported is higher than for Cd^{2+} and Cr^{3+} (Fig. 6). The polymer of TMEAA was used by Djunaidi et al. [21] with the same objective and a similar sequence of Cd^{2+}>Cu^{2+}>>Cr^{3+} was found. Cahyono and Djunaidi [13] synthesized pyridin-2-ylmethyl 2-(eugenoxy)acetate (PMEOA) as a carrier with an N active atom giving transport sequence Cu^{2+}>>Cd^{2+}>Cr^{3+}.

The mass of the carrier compounds used can also affect the amount of metal transport [4]. The result of this research shows that the greater the mass of the carrier compound used, the more metal can be transported. The transport of heavy metals with pH variations is shown in Fig. 7.

Determination of the effect of pH in the stripping phase for metal ion transport using the BLM technique was conducted by varying the pH of HCl in the stripping phase. It can be seen in Fig. 7 that at pH 1.5, Cu^{2+}, Cd^{2+}, and Cr^{3+} were transported in large enough quantities for this pH condition to be used for exploration. In investigating separation among the metal ions pH 1 was used, because at pH 1, Cu^{2+} was transported to a greater extent than Cd^{2+} and Cr^{3+}. Selectivity coefficients of Cu(II)/Cd(II) and Cu(II)/Cr(III) for BLMs decreased with increasing HCl concentration in the stripping phase. The same tendency was reported in the literature [6,22]. The changes of pH in both feed and stripping phases can be seen in Table 1.

CONCLUSION

In the present study, TMEAA can be synthesized from eugenol and can be used as a carrier compound in the BLM technique. The N and S active groups in TMEAA act selectively with Cu^{2+} (borderline) and Cd^{2+} (soft) metal ions.

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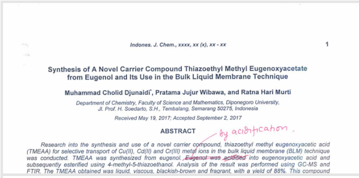

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Synthesis of A Novel Carrier Compound Thiazoethyl Methyl Eugenoxyacetate from Eugenol and Its Use in the Bulk Liquid Membrane Technique

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ABSTRACT

by acidification.

Research into the synthesis and use of a novel carrier compound, thiazoethyl methyl eugenoxyacetic acid (TMEAA) for selective transport of Cu(II), Cd(II) and Cr(III) metal ions in the bulk liquid membrane (BLM) technique was conducted. TMEAA was synthesized from eugenol. ~~Eugenol was acidified~~ into eugenoxyacetic acid and subsequently esterified using 4-methyl-5-thiazoethanol. Analysis of the result was performed using GC-MS and FTIR. The TMEAA obtained was liquid, viscous, blackish-brown and fragrant, with a yield of 88%. This compound

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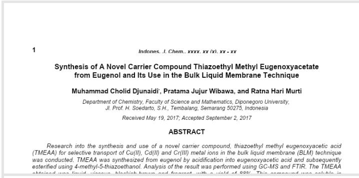

1 Indones. J. Chem., xxxx, xx (x), xx - xx

Synthesis of A Novel Carrier Compound Thiazoethyl Methyl Eugenoxyacetate from Eugenol and Its Use in the Bulk Liquid Membrane Technique

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ABSTRACT

Research into the synthesis and use of a novel carrier compound, thiazoethyl methyl eugenoxyacetic acid (TMEAA) for selective transport of Cu(II), Cd(II) and Cr(III) metal ions in the bulk liquid membrane (BLM) technique was conducted. TMEAA was synthesized from eugenol by acidification into eugenoxyacetic acid and subsequently esterified using 4-methyl-5-thiazoethanol. Analysis of the result was performed using GC-MS and FTIR. The TMEAA

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